ESTIMATION OF THERMODYNAMIC AND TRANSPORT PROPERTIES OF LIQUIDS

Thesis submitted to the

University of Allahabad
for the degree of

DOCTOR OF PHILOSOPHY IN SCIENCE

By

BISHAN DATT BHATT
M. Sc.

Under the supervision of

Prof. J. D. PANDEY
D. Sc.
[Former Head]

Department of Chemistry
University of Allahabad
Allahabad
INDIA

November, 2002

Prof. J. D. PANDEY
D. Sc.

Department of Chemistry
University of Allahabad
Allahabad-211002
U.P., INDIA

CERTIFICATE

This is to certify that **Mr. Bishan Datt Bhatt** has fulfilled all the requirements for the submission of D. Phil. thesis entitled "*ESTIMATION OF THERMODYNAMIC AND TRANSPORT PROPERTIES OF LIQUIDS*" to the University of Allahabad. This is a record of the candidate's own effort under my supervision. This work can be considered as a record of his competence in research work.

Allahabad
November 22, 2002

(J. D. PANDEY)
Supervisor

Residence: 81-A, ALLENGANJ, ALLAHABAD-211002 Ph. : 0532 - 465699

ACKNOWLEDGEMENT

With immense pleasure, I feel it my privilege to express my gratitude to my supervisor, ***Prof. J.D. Pandey***, Former Head, Department of Chemistry, University of Allahabad, for his valuable guidance, dynamic supervision, great motivation, constructive criticisms and progressive suggestions, which enabled me to complete the present work. During the period of my research work, my supervisor was not only just a guide for me, but he also supported me emotionally as a guardian, as a mentor, as a philosopher and as a source of inspiration.

I would like to pay my obscene to the departed soul of ***Late (Mrs) Prabha Pandey***, who, with her mother like behavior always inspired me for the successful completion of the present work.

I am thankful to ***Prof. Bharat Singh***, Head of Department of Chemistry, University of Allahabad, for all the support he provided to me during my research work. I would like to express my deep sense of appreciation to ***Prof. Krishna Mishra***, Department of Chemistry, University of Allahabad for her kind suggestions. I am also equally thankful to ***Prof. Anwar Ali***, Department of Chemistry, JMI University, for his support in my experimental work.

I have deep sense of appreciation to ***Dr. P.N. Pandey***, Department of Mathematics, University of Allahabad, for his guardian like support and encouragement during my stay in Allahabad.

I am grateful to ***Dr. Ranjan Dey***, ***Dr. Vinay Sanguri***, ***Dr. Richa Verma***, ***Mr. Vinod Singh***, ***Dr. S.B. Tripathi*** and ***Dr. Ashish Sharma*** for their

co-operation during my research work. ***Dr. Ranjan Dey*** and ***Dr. Vinay Sanguri*** were teacher-like seniors to me.

I would like to thank my colleagues ***Dr. Amit Pandey***, ***Dr. N.K. Soni***, ***Miss Jyotsna Chhabra***, ***Mr. Rajesh Mishra***, ***Miss Tanuja Nautiyal***, ***Mr. Manoj K. Yadav*** and ***Mr. Arvind K Singh*** for their friendly behavior and co-operation during my research work.

I am thankful to ***Mr. Pramod Singh***, ***Miss Abida***, ***Dr. A.K. Nain***, ***Dr. S. Hyder*** and ***Dr. Y. Akhtar***, for their support during my experimental work.

I would like to thank my ***teachers***, ***friends*** and ***others***, who encouraged me to carry out the present research work.

Finally, I have great sense of appreciation to ***my family members***, who managed to live without my company, during the period of my stay in Allahabad.

Allahabad
November 22, 2002



BISHAN DATT BHATT

PREFACE

Thermodynamic and transport properties of pure liquids and liquid mixtures are gaining enormous amount of interest in recent past due to their applicability in chemical industries for design calculations involving separations, fluid flow, mass transfer, heat transfer, design of condensers and sizing of storage vessels. Ultrasonic velocity, density, refractive index, molar volume, isentropic compressibility, thermal expansion coefficient, internal pressure, thermal conductivity, viscosity and many other derived thermodynamic and transport properties of pure liquids & liquid mixtures are not only the useful properties for a chemical engineer involved in product formulation, but are also useful for a research worker, a physicist or a chemist to study nature of liquids and the molecular interactions. The most important contribution of thermodynamics is to reduce the measurements of a system in equilibrium to the determination of a single thermodynamic function. Many engineering applications require approximate estimates. Simple estimation methods, requiring little input data, are often preferred for the evaluation of various equilibrium properties of the system. Due to the importance of multi-component liquid systems for product formulation in chemical industries, the predictive or estimation methods become even more useful. Realising these facts, the present work has been carried out to enhance the spectrum of such studies and methods for prediction of various thermodynamic and transport properties. Various empirical, semi-empirical, thermodynamic and statistical mechanical theories for the evaluation of a number of thermodynamic and transport properties have been utilised and analysed. Wherever applicable, new approaches for estimation of thermodynamic and transport properties of liquid system, have also been proposed and analysed.

GLOSSARY OF SYMBOLS

Symbol	Meaning
ρ	Density
u	Ultrasonic velocity
n	Refractive index
β_s	Isentropic compressibility
β_s^E	Excess isentropic compressibility
β_s^{id}	Ideal isentropic compressibility
β_T	Isothermal compressibility
γ	Ratio of principal specific heats
α	Thermal expansion coefficient
α^{id}	Ideal thermal expansion coefficient
V	Molar volume
V^{id}	Ideal molar volume
V^E	Excess molar volume
$\tilde{V}$	Reduced molar volume
V^*	Characteristic volume
ϕ_i	Volume fraction of i^{th} component
x_i	Mole fraction of i^{th} component
W_i	Weight fraction of i^{th} component
θ_i	Site fraction of i^{th} component
ψ_i	Segment fraction of i^{th} component
P^*	Characteristic pressure
T^*	Characteristic temperature
$\tilde{T}$	Reduced temperature
C_p	Heat capacity at constant pressure
$\tilde{C}_p$	Reduced heat capacity at constant pressure
C_p^E	Excess heat capacity at constant pressure
R_m	Molar refractivity
ΔR_m	Deviation in molar refractivity from volume fraction average
r	Molecular radius

Symbol	Meaning
B	Geometrical volume
N	Avogadro's number
S	Collision factor
S^*, S_0, S_0^*	Sharma parameters
C_1	Moelwyn-Hughes parameter
F	Huggin's parameter
f	Fractional free volume
K	Isobaric acoustical parameter
K'	Isothermal acoustical parameter
K''	Isochoric acoustical parameter
X	Isochoric coefficient of internal pressure
Γ	Grüneisen parameter
Γ^E	Excess Grüneisen parameter
Γ_G	Psedudo-Grüneisen parameter
δ	Anderson-Grüneisen parameter
B/A	Non-linearity parameter
V_a	Available volume
h	Planck's constant
k	Boltzmann constant
η	Viscosity
V_f	Free volume
ΔG^*	Activation of free energy
ΔG^R	Residual free energy
ΔH_M	Enthalpy of mixing
X_{ij}	Interaction parameter
[R]	Rheochor
λ	Thermal conductivity
P_i	Internal pressure
P_i^E	Excess internal pressure
d	Molecular diameter
σ	Surface tension
H^E	Excess Enthalpy

CONTENTS

CHAPTERS		PAGES
Chapter 1	**Introduction**	**1 –15**
Chapter 2	**Experimental Techniques**	**16 –21**
	2.1 Preparation of solutions	16
	2.2 Measurement of density	16
	2.3 Measurement of ultrasonic velocity	18
	2.4 Measurement of refractive index	19
	2.5 References	20
CHAPTER 3	**Excess volume and excess isentropic compressibility of liquid mixtures**	**22 – 35**
	3.1 Introduction	22
	3.2 Experimental	24
	3.3 Results and Discussion	25
	3.4 References	29
	Tables and Figures	32
CHAPTER 4	**Ultrasonic and refractometric studies of liquid mixtures**	**36 –57**
	4.1 Introduction	36
	4.2 Experimental	38
	4.3 Theoretical	39
	4.4 Results and Discussion	45
	4.5 References	47
	Tables and Figures	50
CHAPTER 5	**Estimation of molecular radii of liquids and liquid mixtures from sound velocity**	**58 -72**
	5.1 Introduction	58
	5.2 Theoretical	59
	5.3 Results and Discussion	61
	5.4 References	62

Tables and Figures 64

CHAPTER 6 **Internal pressure and related properties of liquids and liquid mixtures** **73 - 96**

6.1 Introduction 73

6.2 Theoretical 75

6.3 Results and Discussion 81

6.4 References 83

Tables and Figures 86

CHAPTER 7 **Thermoacoustial, anharmonic, non-linear and related volumetric properties of liquids and liquid mixtures** **97 -116**

7.1 Introduction 97

7.2 Theoretical 99

7.3 Results and Discussion 102

7.4 References 105

Tables and Figures 107

CHAPTER 8 **Evaluation of viscosity of liquids and liquid mixtures** **117 - 136**

8.1 Introduction 117

8.2 Theoretical 119

8.3 Results and Discussion 124

8.4 References 125

Tables 128

CHAPTER 9 **Estimation of thermal conductivity of liquids and liquid mixtures** **137 - 150**

9.1 Introduction 137

9.2 Theoretical 139

9.3 Results and Discussion 140

9.4 References 141

Tables 144

LIST OF PUBLICATIONS **151**

CHAPTER – 1

Introduction

Liquids and especially liquid mixtures are widely used in processing and product formulation in many industrial applications. Thermodynamic and transport properties of the liquids provide useful information about physical forces acting between the molecules of the same substance in pure liquids and molecules of different substances in liquid mixtures. These equilibrium properties are important for liquid mixtures mainly in two ways. One of the interests of studying these properties is to understand the physical forces acting between the molecules and the another aspect is that, there is appearance of new phenomena which are not present in the pure substances. Most important contribution of thermodynamics is to reduce the measurements of a system in equilibrium to the determination of a single thermodynamic function. From the measurements of macroscopic properties, in principle, it is possible to determine the law of force between the molecules[1]. Once the law of force has been determined, it is possible to calculate the equation of state or transport properties. This makes it possible to reduce the description of a great number of equilibrium and non-equilibrium phenomena to a common basis and understand their interrelation from a molecular viewpoint.

The knowledge of thermodynamic and transport properties of multi-component liquid systems is important for design calculations involving separation, fluid-flow, mass transfer, heat transfer, design of condensers, sizing of storage vessels and material & energy balances. The subject of intermolecular forces is important from the viewpoint of its application in many branches of science including molecular biology, polymer science, surface chemistry and colloidal chemistry. A research worker, a physicist or a chemist requires the study of nature of liquids and intermolecular interactions, where thermodynamic and transport properties become significant.

When two liquids are mixed together, the resulting changes in physical and thermodynamic properties can be considered as a sum of several contributions, due to free volume change, change in energy, change in molecular orientations

and steric hindrances. The equation of state and the transport properties are intimately related to the forces between the molecules[1]. The intermolecular forces can be basically classified in two types: - (a) Short-range (or valence or chemical) forces, which arise when molecules come closer and their electron clouds overlap. These forces are repulsive in nature and often highly directional (b) Long-range forces, which depend upon intermolecular separations. Long-range contributions are divided into three parts viz. electrostatic contribution, induction contribution and dispersion contribution. For convenience, arbitrarily the important intermolecular forces may be classified as[2]:

a) Electrostatic forces between charged particles and between permanent dipoles or quadrupoles, and higher multipoles.
b) Induction forces between a permanent dipole and an induced dipole.
c) Dispersion forces and repulsion between non-polar molecules.
d) Specific (Chemical) force leading to association and complex formation (e.g. hydrogen bonding).

Physical, thermodynamic and acoustic properties are affected by the intermolecular hydrogen bonding, dipole interactions, dipole-induced dipole interactions and charge transfer interactions between unlike molecules owing the variation in concentration of one of the components[3], when the substances are mixed together. Moelwyn-Hughes[4], Hildebrand[5], Marcus[6], Kihara[7] and Murrel[8] have given details about intermolecular forces. Both experimental observations and theoretical approaches are important for the knowledge of intermolecular forces. Theory suggests the functional form of the potential of interaction, whereas, the adjustable parameters of the potential function are empirically determined by the experimental data. As experimentally measured macro properties need to have high degree of accuracy for the above-mentioned purpose, most of the information about the intermolecular forces is obtained from the properties of dilute gases and crystals. Experimentally observed properties are

important for the molecular level interpretations. For example, ultrasonic velocity and density data can be utilised to study the intermolecular arrangement of the liquid. As thermodynamic properties which are not directly obtained by other means, can be determined using these data, one can easily understand their importance. But even with today's advancements in the instrumentation, experimental measurements of some of the properties are either impossible or difficult and time consuming.

Due to importance of multi-component liquid systems in product formulation in chemical industries, some predictive methods for the evaluation of properties in liquid mixtures have gained enormous interest. Many engineering applications require approximate estimate and simple estimation methods requiring little or no input data is often preferred. Very simple and convenient methods, for example, estimation of density by additive method, proposed by Schroeder[9] may even be important. Group contribution method is another example of methods of estimating the thermodynamic and transport properties of pure liquids and liquid mixtures with the use of nearly no input data, except the knowledge of the structure of the molecule. Even the values of viscosity, ratio of specific heats, surface tension and heat capacity can be predicted using group contribution methods. The group contribution methods have been extensively discussed by Reid et al[10]. Law of corresponding states, proposed by van der Waals[10], is another approach to estimate the properties of pure liquids and liquid mixtures, using minimum input data especially the critical constants. This law expresses the generalisation that equilibrium properties, which depend upon the intermolecular forces, are related to the critical properties in a universal way. Use of various mixing rules for the evaluation of various thermodynamic and transport properties of liquids mixtures are also very useful methods of prediction.

Thermodynamic excess functions give the idea about the extent to which real mixtures deviate from ideality. Various excess functions have been extensively

discussed by Rowlinson and Swinton[11], in condensed gases, liquefied natural gaseous mixtures, mixtures of hydrocarbons, mixtures containing metal halides, mixtures containing polar liquids and aqueous mixtures. The various approaches for the determination of excess thermodynamic quantities have been discussed by Douheret et al[12, 13]. Guggenheim[14] studied the excess thermodynamic properties in non-electrolytes.

Various theories/models proposed to describe the liquid state, in different ways, provide relations, which can be used to evaluate thermodynamic and transport properties of the liquids and liquid mixtures. Good approximations are provided by the regular solution theory[16,17] in non-polar liquids. This theory assumes that in regular solutions, components mix with no excess entropy provided that there is no volume change upon mixing. The Lattice theory, which was initially proposed by Eyring and co-workers[18], was extended later on after some simplifications[19-20], considers liquid to be solid-like in quasi-crystalline state, where molecules do not translate fully in chaotic manner as in gas. Perhaps the simplest model is the "cell" or "free volume" model, which supposes a molecule to be confined to small region of the liquid by the effect of repulsive fields of its neighbours. There is theoretical evidence that, such a treatment should work best for a closed-packed liquids[21]. Assumptions regarding free volume theory that there are probabilities of occurrence of empty neighbouring sites in liquids, where molecules can jump[23], have been useful in the study of viscosity of liquids and liquid mixtures. The Absolute Rate Theory[24] describes about free energy needed for a molecule to jump to a new equilibrium position. The concept[25] of combining free volume theory and absolute rate theory has been useful for the deduction of relation for evaluation of viscosity.

Statistical thermodynamics provides relationships between macroscopic properties and intermolecular forces through partition functions, very much concerned with [illegible] prediction of bulk properties. In recent past, statistical mechanical

theories have become progressively important for the liquids and liquid mixtures. Hirschfelder[1], Prausnitz[2] and Acree[26] have discussed the statistical mechanical models of fluids. Theories like scaled particle theory[27] assumes that all molecules are rigid, and that, internal molecular degrees of freedom (rotation or vibration) are not changed by the dissolution process[2]. This assumption is reasonable only for small spherical molecules. For non-spherical molecules, the solute-solvent interaction forces contribute to the entropy. One of the statistical-mechanical theories, which uses a number of molecular parameters for its application is Significant Structure Theory (SST). This theory was developed by Eyring and his group[28-30]. This theory has been utilised[31-33] in liquids and liquid mixtures successfully, to predict thermodynamic and transport properties. Flory statistical theory (FST)[34-38] has gained enormous interest in recent past to evaluate various thermodynamic and transport properties owing its simplicity and validity. Flory theory was initially proposed for thermodynamic properties of n-alkanes and was subsequently extended for non-polar molecules differing in size and shape, and has been applied to system of simple and complex liquid mixtures. In recent past, this theory has been applied[32,39-45] for the evaluation of a number of thermodynamic and transport properties with some adjustments or in conjunction with the relations from other theories as well.

The extensive application of Flory statistical theory is due to its simplicity in the use and precisions in the prediction of various thermodynamic and transport properties. In most of the cases, the approach requires only thermal expansion coefficient (α) and isothermal compressibility (β_T) data of pure liquids for the evaluation of various thermodynamic and transport properties of liquid mixtures. The attempts of using this theory in conjunction with the use of empirical and semi-empirical relations have even been found to be useful.

Sound velocity at very low frequencies and its dependence on temperature are connected with the properties of liquids. Low frequency values of sound velocity

can be considered as thermodynamic property[21] i.e. they are independent of any knowledge of microscopic structure of the liquid. Thermodynamics can be considered as a tool to connect it with many other properties of the liquids. Ultrasonic technique has been found to be most important tool for the structural and interaction studies of liquids and liquid mixtures. Ultrasonic velocity and density data in conjunction with P-V-T equation provide very useful information about the liquid mixtures also, which are useful to study molecular interactions. Another important and easily measurable parameter of liquids and liquid mixtures, is refractive index. This property is also very useful in the sense that, this property is related with other properties of the solution like molar refractivity, dielectric constant and viscosity.

The ultrasonic velocity (u), density (ρ) and refractive index (n) data can on the other hand be utilised to evaluate the properties of the mixtures like excess molar volume (V^E), isentropic compressibility (β_S), excess isentropic compressibility ($\beta_S{}^E$), Molar refractivity (R_m), deviations of molar refractivity from volume fraction average (ΔR_m), molar sound velocity (R) and deviations of molar sound velocity from volume fraction average volumes (ΔR). These Properties are related with other properties of the liquids and liquid mixtures. They also provide a useful mean of studying intermolecular interactions in liquid mixtures, which are very useful in chemical industries and in research work. Many workers[46-55] have carried out experiments on determination of ultrasonic velocity, density and refractive index in recent past. The experimentally obtained values of these various properties can by used to test the theories/relations for the prediction of these properties like Flory theory[34-38], Van Dael and Vangeel relation[56], Nomoto Relation[57], Junjie Relation[58], Collision Factor Theory[59], Gladstone-Dale relation [60], Lorentz-Lorenz relation[61], Eykman relation[62], Weiner relation[63], Heller relation[64] and Newton relation[65]. Many workers in recent past[66-71] have used the excess properties and deviations in properties from the volume fraction average for the interpretation of molecular interactions in liquid mixtures. The use of Flory

statistical theory for the evaluation of ultrasonic velocity in liquid mixtures, however, is almost limited to the use of empirical relations in conjunction with the statistical theories, in the previous studies.

Molecular radius is one of the important parameters of the liquids and liquid mixtures as it is a required parameter for the evaluation of many other properties[25,59] of the liquid system. Several relations are available in literature[59,72-75] for the evaluation of molecular radius of liquids. Though, the variation pattern in molecular radius data with some parameters of liquids, by various methods has been studied[76], the comparative study of various methods for evaluation of molecular radius in liquid mixtures, has not been not found in the literature. The studies of interrelation between the molecular radius and other related properties also are scarce.

Internal pressure is one of the important fundamental properties of the liquid state, which finds its extensive application in study of molecular interactions. Hildebrand et al[77], Barton[78] and Dack[79] made pioneer attempt on the study of internal Pressure. Internal Pressure of liquids is related with a number of parameters of liquid state like pseudo-Gruneisen parameter, solubility parameter and excess enthalpy. Internal pressure provides a measure of explaining molecular interaction, internal structure, clustering phenomenon ionic interaction and dipolar interaction. Some empirical relations for the evaluation of internal pressure on the basis of viscosity, density & ultrasonic data[80], hard-sphere diameter[81] and ultrasonic velocity & density data[82] are available. Internal pressure and related parameters in liquids and liquid mixtures have been studied by several workers in recent past[39,83-85]. But comparative studies of all these sort of relations alongwith thermodynamic relations, has not been found in literature. Use of Flory statistical theory, without the application of any empirical relation, has not also been practiced by previous workers.

Most of the thermoacoustical, anharmonic, non-linear and related volumetric properties can be computed using minimum input data, mostly, the thermal expansion coefficient (α). The important studies in these regards were made by Sharma[86-89] and these properties are studied in various organic compounds at various conditions by Pandey et al[90]. Tabhane et al[91] studied some of these properties in liquid mixtures. As liquids support quasi-crystalline model for their structure, the properties, which had been applied to study solid crystalline state, have now days been applied to liquid state also. The concept of pseudo-Gruniesen parameter is being applied to the liquid mixtures also. Similarly the parameters like Moelwyn-Hughes parameter, Sharma parameters, Isobaric acoustical parameter, isothermal acoustical parameter, isochoric acoustical parameter and Anderson-Gruneisen parameter are useful to compute other properties of liquids.

Viscosity and thermal conductivity in pure liquids and liquids mixtures are very useful transport properties. Viscosity is used commonly in product designing and optimization in many chemical industries and thermal conductivity finds its extensive use especially in the industries using refrigerants. The difference between transport properties in gas phase and liquid phase indicate a distinct change in mechanism of energy or momentum transfer. Transfer of momentum in gas phase in due to collision mechanism, while in liquid phase, the mechanism is of oscillation type. Various theories of liquid system explain the relation for evaluation of viscosity in different ways. The concepts of Bloomfield & Dewan[92], Grunberg & Nissan[93], Wassiljewa[94], Bingham[95], Kendal-Munroe[96], McAllister[97], are some well known methods. There are some other methods for evaluation of viscosity of pure liquids and liquid mixtures. The best advantage of these methods is that they require minimum input data, especially the viscosities of pure liquids, for the evaluation of viscosities of liquids mixtures. Many relations for the estimation of thermal conductivity of fluids have been extensively discussed by Reid et al[10]. Most of these methods are based upon the corresponding state correlations. These methods will not be discussed individually here, some of

which are Sato-Reidel method[10], Wasssiljewa method[94], and Li method[98]. Pandey et al[99-100] have used Flory theory in conjunction with Hirschfelder et al[1] concept to evaluate thermal conductivity in some simple liquids. Tremendous amount of work has been carried out by several workers in the determination and estimation of viscosity of pure liquids and liquids mixtures. It is not possible to include all these studies here. In recent past also, viscometric studies in liquids systems have been significantly reported in literature [32,48,101-106].

The present work entitled "Estimation of thermodynamic and transport properties of liquids" has been reported in nine chapters. Chapterwise summary of the work is outlined here.

Chapter 1 of this thesis is introductory chapter. This chapter deals with the literature survey, scope of the work and brief theoretical details of thermodynamic and transport properties of pure liquids & liquids mixtures.

Chapter 2 deals with the experimental techniques applied for the experimental measurements of density, ultrasonic velocity and refractive index. The method of solution preparation, methods used for calibration and brief instrumentation are described in this chapter.

Chapter 3 deals with the application of experimental ultrasonic velocity and density data of liquid mixtures, to evaluate isentropic compressibility and excess molar volume. The liquid mixtures under investigation are binary liquid mixtures of ethanol + N,N-dimethylformamide (N,N-DMF), N,N-DMF + cyclohexane & ethanol + cyclohexane, and ternary liquid mixture of ethanol + N,N-DMF + cyclohexane. This chapter also reports the use of Flory statistical theory for the evaluation of isentropic compressibility without the use of any empirical relations, as a new approach.

Chapter 4 deals with the application of experimental ultrasonic velocity, density and refractive index data of the binary liquid mixtures - ethanol + N,N-DMF, ethanol + cyclohaxane & N,N-DMF + cyclohexane and ternary liquid mixture - Ethanol + N,N-DMF + cyclohexane, to evaluate properties like molar refractivity, its deviation from volume fraction average, molar sound velocity and deviation of molar sound velocity from volume fraction average values. Validation of predictive rules/ relations for the evaluation of refractive index and ultrasonic velocity of liquid mixtures has also been reported. The use of Flory statistical theory[34-38] without the application of any empirical relation has also been reported, as a new approach.

Chapter 5 deals with the theoretical methods for the evaluation of molecular radius in a number of pure organic liquids and a number of liquid mixtures of organic compounds. Various relations for the evaluation of molecular radius, in liquid system have been reported with their relative merits.

Chapter 6 deals with the theoretical methods for the evaluation of internal pressure in a number of pure organic liquids and many liquids mixtures of organic compounds. The application of Flory Statistical Theory[34-38] without the use of any other empirical relations, to evaluate internal pressure has also been reported, as a new approach in this chapter.

Chapter 7 deals with the theoretical methods for the evaluation of various thermoacoustical, anharmonic, non-linear and related volumetric properties in a number of organic liquids and many liquid mixtures of organic compounds, with the use of minimum input data, especially thermal expansion coefficient (α) . The applicability of thermoacoustical parameters for the evaluation of available volume has also been reported, as a new approach.

Chapter 8 deals with the theoretical methods for the prediction of viscosity in liquid mixtures of various organic compounds with the help of some well-known methods. Use of Flory statistical theory[34-38] without the use of any empirical relation and Grunberg-Nissan method[93] in conjunction with group contribution method have been reported, as new approaches. Along with these methods, a new relation proposed by author has also been reported.

Chapter 9 of this thesis encompasses theoretical methods for the evaluation of thermal conductivity of some pure organic liquids and some organic liquid mixtures. Use of Wassiljewa relation[94] for ***organic liquid mixtures*** and Sato-Riedel Method[10] in conjunction with group contribution method for pure organic liquids have also been reported, as a new approach.

References

1. Hirschfelder J O, Curtiss C F & Bird R B, *Molecular Theory of Gases and Liquids*, John Wiley & Sons Inc, New York, 1964.
2. Prausnitz J M, Lichtenthaler R N & deAzevedo E G, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd Ed, Printice-Hall Inc, N J, 1985.
3. Fort R J, & Moore W R, *Trans Farad Soc*, **61** (1965), 2102; **62** (1966) 1112.
4. Moelwyn-Hughes E A, *Physical Chemisty*, Perganon Press, Oxford, 1961.
5. Hildebrand J H, Prausnitz J M & Scott R L, *Regular Solutions*, Van Nostrand Reinhold Co, New York, 1970.
6. Marcus Y, *Introduction to Liquid State Chemistry*, John Wiley & Sons Ltd, 1977.
7. Kihara T, *Intermolecular Forces*, John Wiley & Sons, New York, 1978.
8. Murrel J N & Jenkins A D, *Properties of Liquids and Solutions*, John Wiley & Sons, 2nd Ed, England, 1994.
9. Partington J, *An Advanced Treatise on Physical Chemistry*, Vol-2, New York, 1950.

10. Reid R C, Prausnitz J M & Poling B E, *The Properties of Gases and Liquids*, McGraw-Hill Inc, 4th Ed, 1987.

11. Rowlinson J S & Swinton F L, *Liquids and Liquid Mixtures*, Butterworth Scientific, 3rd Ed, 1982.

12. Douheret G, Moreau C, Viallard A, *Fluid Phase Equilibria*, **22** (1985) 289; **22** (1985) 277.

13. Douheret G & Viallard A, *J Chem Phys*, **8** (1983) 809.

14. Guggenheim E, *Mixtures*, The Corendon Press, Oxford, 1952.

15. Kiyohara O, Halpin C J & Benson G C, *J Chem Thermodyn*, **10** (1978) 721.

16. Scatchard G, *Chem Rev*, **44** (1949) 7

17. Hidebrand J H, *J Am Chem Soc*, **51** (1929) 66.

18. Eyring J H & John M S, *Significant Liquid Structures*, John Wiley & Sons Inc, New York, 1969.

19. Guggenheim E A, *Application of Statistical Mechanics*, Oxford Univ Press, Oxford, 1966.

20. Baker J A, *Lattice Theories of the Liquid State*, MacMillan Publishing Company, N Y, 1963.

21. Temperley H N V, Rowlinson J S & Rushbrooke G S, *Physics of Simple Liquids*, North- Holland Publishing Co, Amsterdam, 1968.

22. Williams M L, Landel R F & Ferry J D, *J Chem Soc*, **77** (1955) 3701.

23. Cohen M H, Turnbull D, *J Chem Phys*, **31** (1956) 1164.

24. Glasstone S, Laidler K J & Eyring H, *The Theory of Rate Processes*, McGrawHill, New York, 1941.

25. Macedo P B & Litovitz T A, *J Chem Phys*, **42** (1965) 669.

26. Acree W E (Jr), *Thermodynamic Properties of Non-electrolyte Solutions*, Academic Press, Orlando, 1984.

27. Reiss H , Frisch H L, Helfand E & Lebowitz J L, *J Chem Phys*, **32** (1960) 33; **119** (1960) 1379.

28. Eyring H & John M S, *Significant Liquid Structures*, John Wiley & Sons Inc, New York, 1969.

29. Fuller E J, Ree T & Eyring H, *Proc Natl Acad Sci (USA)*, **45** (1959) 1594.

30. Eyring H & Ree T, *ibid*, **47** (1961) 526.

31. Pandey J D & Gupta U, *Electrochim Acta*, **29 (3)** (1984) 403.

32. Pandey J D, Pandey S, Gupta S & Shukla A K, *J Soln Chem*, **23(9)** (1994) 1049.

33. Pandey J D, Shukla A K, Shikha & Tripathi N, *Ind J Chem*, **33A** (1994) 613.

34. Flory P J, Orwoll R A & Vrij A, *J Am Chem Soc,* **86** (1964) 3507.

35. Flory P J, *J Am Chem Soc,* **87** (1965) 1833.

36. Flory P J & Abe A, *ibid*, **86** (1964) 3563.

37. Abe A & Flory P J, *J Am Chem Soc,* **87** (1965) 1838.

38. Flory P J, Orwoll R A & Vrij A, *ibid,* **86** (1964) 3515.

39. Pandey J D, *J Chem Soc Farad Trans*, **76** (1980) 1215.

40. Pandey J D, Shukla R K, Shukla A K & Rai R D, *J Chem Soc Farad Trans*, **84** (1988) 1853.

41. Pandey J D, Rai R D & Shukla R K, *J Chem Soc Farad Trans,* **85** (1989) 331.

42. Pandey J D, Shrivastava V N, Vyas V & Pant N , *Ind J Pure & Appl Phys,* **25** (1987) 467.

43. Islam M R & Quadri S K, *Acoustics Letters*, **11** (1988) 237.

44. Khanwalkar M S, Murty J S & Despande D D, *Acoustics Letters,* **13(7)** (1990) 121.

45. Pandey J D & Dey R , *Ind J Phys*, **74 A** (2000) 319.

46. Ali A & Nain A K, *J Pure & Appl Ultroson*, **22** (2000) 10.

47. Pandey J D, Haroon S, Dubey K K , Upadhyaya M, Dey R and Mishra K, *Can J Chem*, **78** (2000) 1561.

48. Aminabhavi T M & Banerjee K, *Ind J Chem*, **40 A** (2001) 53.

49. Hiroyuki O, *J Chem Thermodyn*, **34 (6)** (2002) 849.

50. Comeli F, Francisconi S O & Castellari C, *J Chem Eng Data*, **47(5)** (2002) 1226.

51. Pal A & Bhardwaz R K, *J Chem Thermodyn*, **34(8)** (2002) 1157.

52. Resa J M, Gonzalez C, Landaluc S O & Lanz J , *J Chem Thermodyn*, **34(7)** (2002) 1013.

53. Gomez - Diaz D, Mejuto J C & Navaza J M, *J Chem Eng Data*, **46** (2001) 720.

54. Aznarez S, Katz M & Arancibia E L, *J Soln Chem*, **31 (8)** (2002) 639.

55. Taboada M E, Veliz D M, Galleguillous H R, & Graber T A, *J Chem Eng Data*, **47 (5)** (2002) 1123.

56. Van Dael W & Vangeel E, *Proc 1st Int conf on calorimetry and Thermodynamics*, Warsaw, 1969.

57. Nomoto O, *J Phys Soc Jpn*, **13** (1958) 1528.

58. Junjie Z, *J Chem Uni Sci Tech*, **14** (1984) 298.

59. Schaaffs W, *Z Physik*, **114** (1939) 110.

60. Dale D & Gladstone F, *Philos Trans R Soc Lond*, **148** (1958) 887.

61. Lerentz H A, *Weid Ann*, **9** (1980) 641; Lorenz L, Weid Ann, **11**(1980) 70.

62. Bottcher C F J, *Theory of Electric Polarization*, Elsevier, Amsterdam, 1952.

63. Weiner O, *Leipz Ber*, **62** (1910) 256

64. Heller W, *Phys Rev*, **68** (1945) 5.

65. Kurtz S S & Ward A L, *J Franklin Inst*, **222** (1936) 563.

66. Diaz C, Org B, Marino G & Tojo J, *J Chem Thermodyn*, **33(9)** (2001) 1015.

67. Pal A & Bhardwaj R K, *J Chem Eng Data*, **47(5)** (2002) 1128.

68. Naejus R, Damas C, Lemordant D, Coudert R & Willmann P, *J Chem Thermodyn*, **34 (6)** (2002) 795.

69. Peleteiro J, Gonzalez D, Cerdeirina C A & Romani L, *J Chem Thermodyn*, **34(4)** (2002) 485.

70. Aralaguppi M I, Aminabhavi T M, Harogoppad S B & Balundgi R H, *J Chem Eng Data*, **37** (1992) 298.

71. Aminabhavi T M, Phayde H T S, Khinnavar S & Gopalkrishna B, *J Chem Eng Data*, **39** (1994) 251.

72. GopalaRao R V & Venkataseshaiah V, *Z Phys Chem*, **242** (1969) 193.

73. Kincaid J F & Eyring H, *J Chem Phys*, **5** (1937) 587.

74. Kittel C, *J Chem Phys*, **14** (1946) 614.

75. Glasstone S, *Text Book of Physical Chemistry*, MacMillan & Co Ltd, London, 1962.

76. Ernst E & Glinski J, *Acustica*, **13** (1981) 109.

77. Hildebrand J H & Scott R L, *Solubility of Non-electolytes*, Reinhold, New York, 1964.

78. Barton A F M, *J Chem Edu*, **48** (1971) 156; *Chem Rev*, **75** (1975) 731.

79. Dack M R, *J Chem Soc Rev* (GB), **4** (1975) 211.

80. Suryanarayana C V, *Ind J Pure & Appl Phys*, **27** (1989) 751.

81. Buehler R J, Wentorff R H, Hirschfelder J O & Curtiss C F, *J Chem Phys*, **19** (1951) 61.

82. Singh A K, D Phil Thesis, University of Allahabad, 1995.

83. Pandey J D, Shukla A K, Tripathi N & Dubey G P, *Pramana: J Phys*, **40** (1993) 81.

84. Aminbhavi T M, Banerjee K & Balundgi R H, *Ind J Chem*, **38 A** (1999) 768.

85. Arul G & Palaniappan L, *Ind J Pure & Appl Phys*, **39** (2001) 561.

86. Sharma B K , *Acustica,* **45** (1980) 65.

87. Sharma B K, *Acoust Soc Ind*, **4** (1984) 20.

88. Sharma B K, *J Acoust Soc Am,* **73 (1)** (1983) 106.

89. Sharma B K, *Ind J Pure & Appl Phys*, **25** (1987) 262.

90. Pandey J D, Dubey G P & Dey R, *Acustica-acta-acustica*, **83** (1997) 90.

91. Tabhane V A, Ghosh S & Agrawal S, *J Pure & Appl Ultrason*, **21** (1999) 122.

92. Bloomfield V A & Dewan R K, *J Phys Chem*, **75** (1971) 3113.

93. Grunberg L & Nissan A H, *Nature*, **164** (1949) 799.

94. Wassiljewa A , *Phys* J, **5** (1904) 737.

95. Bingham E C, *Fluidity and Plasticity*, McGrawHill, New York, 1992.

96. Kendall J & Munroe K P, *J Am Chem Soc*, **39** (1917) 1787.

97. McAllister R A, *AIChE J*, **6** (1960) 427.

98. Li C C, *AIChE J*, **22**(1976) 927.

99. Pandey J D, Chaturvedi B R & Pant N, *Acoustics Letters*, **4 (7)** (1981) 128.

100. Pandey J D & Dey R, *Ind J Phys*, **74A** (2000) 319.

101. Martinez S, Garriga R, Perez P & Gracia M, *Fluid Phase Equilibria*, **168** (2000) 267.

102. Tu C, Lee S & Peng I, *J Chem Eng Data*, **46** (2001) 151.

103. Cruz R C, Martins R J, Cardoso M J & Barcia O E, *J Chem Eng Data*, **47(4)** (2002) 927.

104. Victor P J & Hazra D K, *J Chem Eng Data*, **47** (2002) 79.

105. Manfredini M, Merchetti A, Sighinolfis, Tessi L, Ulrici A, Vignoli M & Zucchi C, *J Soln Chem*, **31(3)** (2002) 235.

106. Marigliano A C & Solimo H N, *J Chem Eng Data*, **47(4)** (2002) 796.

CHAPTER - 2

Experimental Techniques

This chapter deals with the experimental techniques used for the measurements of density, ultrasonic velocity and refractive index of liquids and liquid mixtures.

2.1 Preparation of Solutions

BDH, Ranbaxy and E. Merck (AR) grade organic liquids and triply distilled water were used for the calibration and measurements of density, refractive index and ultrasonic velocity. Organic liquids used for the purpose were purified by distillation, and the purity of such liquids was ascertained by measuring density and ultrasonic velocity of the liquids. The results thus obtained were compared with literature values. The volumes of components required for preparing the solutions of known composition were calculated. The solutions were prepared by taking the calculated amounts by volume but mole fractions of such solutions were calculated by considering the mass of components, to get more accuracy in the mole fraction values. Ternary liquid mixtures were prepared by preparing a pseudo-binary liquid mixture of a particular mole fraction ratio of two components, and taking different amounts of third component. The mole fractions, in this case, were also calculated by considering the mass of the components taken. Liquid mixtures, thus prepared, were labelled and stored in dry place in airtight bottles to avoid the loss of liquid and change of composition of liquid mixture with time.

2.2 Measurement of Density

Densities of the systems under investigation were measured using single-limbed pyknometer with a bulb capacity of approximately 10^{-5} m^3 volume. The stem of pyknometer contained uniform gradation of 10^{-8} m^3 volume, marks of which were calibrated using triply distilled water. In order to maintain constant temperature, thermostatically controlled water bath with precision ±0.05 K was used. Several workers[1-9] have used pyknometer for the measurement of density of liquids. In recent past also[10-13], the measurements of densities of liquids and liquid mixtures have gained enormous interest.

Calibration of Pyknometer

Pyknometer was calibrated using triply distilled water as a standard solvent. The marks of the stem of the pyknometer were calibrated using the procedure described in literature[3]. The volume of liquid between two marks (Δv) can be calculated from number of marks between two different liquid layers (Δn), weights of liquids which are filled up to two different levels (w_1 and w_2) and reference density (ρ_{ref}) as:

$$\Delta v = \frac{(w_2 - w_1)}{\rho_{ref}.\Delta n}$$

Density of liquid (ρ) was calculated from the values of volume of liquid up to reference mark (v), number of marks above the reference mark (Δx) and mass (m) was calculated as:

$$\rho = \frac{m}{v + (\Delta x.\Delta v)}$$

The reproducibility in the measurement of density was at ± 0.01 kg m^{-3}. The experimental values of density were found to be in good agreement with the literature values. The experimental and literature values of density of various liquids at 308.15 K are given in table-1.

Table-1

Experimental and literature values of density (ρ) at 308.15 K

	ρ (kg m^{-3})		
Liquids	**Experimental**	**Literature**	**Reference**
Water	994.2	994.1	13
N, N-dimethylformamide	935.5	935.7	14
1,4-Dioxan	1014.8	1015.6	15
Toluene	852.8	852.9	15
Benzene	863.8	863.1	15
Cyclohexane	764.2	764.4	14
Ethanol	777.9	777.6	14
Hexane	645.0	644.7	9

2.3 Measurement of ultrasonic velocity

Ultrasonic velocity was measured at a fixed frequency of 2 MHz using ultrasonic interferometer, supplied by Mittal Enterprises (New Delhi). This instrument contains two major parts viz. high frequency generator and the measuring cell. The former is designed to excite the transducer, which generates ultrasonic waves in experimental liquid, and the later one serves as coupler between the quartz crystal fixed at the bottom of measuring cell and the high frequency generator. Several workers[2,4,8,9,16-22] have used ultrasonic interferometer to measure ultrasonic velocity. In recent past also[23-25], the measurements of ultrasonic velocity of liquids and liquid mixtures have gained enormous interest.

Method of Calculation

Ultrasonic velocity (u) can be calculated using frequency of acoustic vibration (f) and wave length of waves in medium (λ) as:

$$u = f \times \lambda \qquad ...(1)$$

The distance traveled by the micrometer between two successive maxima (of anodic current) is half of the wavelength, and if n is the number of maxima recorded, then

$$d = n(\lambda/2)$$

or, $$\lambda = 2d/n \qquad ...(2)$$

From eqs (1) and (2),

$$u = 2fd/n \qquad ...(3)$$

For the current investigation, 14 maxima were recorded in each case (n=14) and the operating frequency of interferometer was 2 MHz. Equation (3) for this particular case becomes

$u = d \times 2 \times 10^6 / 7$ ms^{-1}, where d is in meters.

Table-2

Experimental and literature values of ultrasonic velocity (u) at 308.15 K

	u ($m\ s^{-1}$)		
Liquids	**Experimental**	**Literature**	**Reference**
Water	1519.14	1519.36	13
N,N-dimethylformamide	1432.00	1428.50	14
1,4-dioxan	1300.10	1299.00	15
Toluene	1264.82	1265.00	15
Benzene	1250.00	1248.00	15
Cyclohexane	1209.14	1209.10	14
Ethanol	1117.46	1117.00	14
Chlorobenzene	1228.00	1226.00	15

2.4 Measurement of refractive index

Abbe's Refractometer was used for the measurement of refractive indices of various systems under investigation. The instrument has been used by several workers[20,26-28] to measure refractive index. In recent past also[29-33], the measurements of densities of liquids and liquid mixtures have gained enormous interest. Light source contained sodium light of wavelength 589 nm. Triply distilled water was used for the calibration of the instrument. The liquid used for the calibration was placed on the prism of refractometer and prism was almost immediately closed to avoid the escape of liquid by evaporation. Reading according to the literature value was set which was read by analog readout. Liquid was observed through eyepiece and calibration screw was rotated up to a point, where shadow line was centered in the crosshairs.

The resolution of the instrument used was 0.001. The measured and reference values of refractive index for some liquids are given below in table-3.

Table-2

Experimental and literature values of ultrasonic velocity (u) at 308.15 K

	u ($m\ s^{-1}$)		
Liquids	**Experimental**	**Literature**	**Reference**
Water	1519.14	1519.36	13
N,N-dimethylformamide	1432.00	1428.50	14
1,4-dioxan	1300.10	1299.00	15
Toluene	1264.82	1265.00	15
Benzene	1250.00	1248.00	15
Cyclohexane	1209.14	1209.10	14
Ethanol	1117.46	1117.00	14
Chlorobenzene	1228.00	1226.00	15

2.4 Measurement of refractive index

Abbe's Refractometer was used for the measurement of refractive indices of various systems under investigation. The instrument has been used by several workers[20,26-28] to measure refractive index. In recent past also[29-33], the measurements of densities of liquids and liquid mixtures have gained enormous interest. Light source contained sodium light of wavelength 589 nm. Triply distilled water was used for the calibration of the instrument. The liquid used for the calibration was placed on the prism of refractometer and prism was almost immediately closed to avoid the escape of liquid by evaporation. Reading according to the literature value was set which was read by analog readout. Liquid was observed through eyepiece and calibration screw was rotated up to a point, where shadow line was centered in the crosshairs.

The resolution of the instrument used was 0.001. The measured and reference values of refractive index for some liquids are given below in table-3.

Table-3

Experimental and literature values of refractive index (n) at 308.15 K

Liquids	n		
	Experimental	**Literature**	**Reference**
Water	1.332		
N,N-dimethylformamide	1.423		
Toluene	1.489	1.487	17
Benzene	1.494	1.492	17
Cyclohexane	1.420	1.419	23
Ethanol	1.357		
Dimethyl sulphoxide	1.470	1.473	17

2.5 References

1. Pandey J D & Shukla A, *Acoustics Letters*, **9(10)** (1986) 156.
2. Nath J, *J Chem Thermodyn*, **28** (1996) 481.
3. Nain A K, Ali A & Alam M, *J Chem Thermodyn*, **30** (1998) 1275.
4. Sastry N V, Patel M C & Patel S R, *Fluid Phase Equilibria*, **155** (1999) 261.
5. Pandey J D & Haroon S, Dubey K K, Upadhyaya M, Dey R & Mishra K, *Can J Chem*, **78** (2000) 1561.
6. Ali A & Nain A K, *J Pure & Appl Ultrason*, **22** (2000) 10.
7. Pal A, Sharma S & Kumar A, *Ind J Pure & Appl Phys*, **38** (2000) 174.
8. Arul G & Palaniappan L, *Ind J Pure & Appl Phys*, **39** (2001) 561.
9. Aminabhavi T M & Banerjee K, *Ind J Chem*, **40A** (2001) 53.
10. Hiroyuki O, *J Chem Thermodyn*, **34(6)** (2002) 849.
11. Scharlin P, Steinby K & Domaska U, *J Chem Thermodyn*, **34(6)** (2002) 927.
12. Comeli F, Francesconi S O & Castellari C, *J Chem Eng Data*, **47(5)** (2002) 1226.
13. Victor P J & Hazra D K, *J Chem Eng Data*, **47** (2002) 79.
14. Ali A, Nain A K & Kamil M, *Thermochemica Acta*, **274** (1996) 209.
15. Deshpande D D & Bhatgadde L G, *J Phys Chem*, **72** (1968) 261.

16. Low D I R & Moelwyn-Hughes E A, *Roy Soc Lond*, **267** (1962) 384.
17. Rajgopal E & Subramanyam S V, *J Chem Thermodyn*, **12** (1980) 797.
18. Sachadeva V K & Nanda V S, *J Chem Phys*, **75(9)** (1981) 4745.
19. Oswal S L & Palsanwala P P, *Acoustics Letters*, **13** (1989) 66.
20. Aralaguppi M I, Aminabhavi T M, Harogoppad S B & Balundgi R H, *J Chem Eng Data*, **37** (1992) 298.
21. Aminabhavi T M, Khinnavar R S, Phayde H T & Bindu G, *Ind J Chem Technol*, **1** (1994) 343.
22. Nath J & Dubey S N, *J Chem Phys Chem*, **17** (1980) 2166.
23. Pal A & Bhardwaz R K, *J Chem Thermodyn*, **34(8)** (2002) 1157.
24. Dutour S, Lagourette B & Daridon J L, *J Chem Thermodyn*, **34(4)** (2002) 475.
25. Resa J M, Gonzalez C, Landaluce S O & Lanz J, *J Chem Thermodyn*, **34(7)** (2002) 1013.
26. Oswal S L & Palsanawala P P, *Acoustics Letters*, **13(4)** (1989) 66.
27. Nath J & Chaudhary S K, *J Chem Eng Data*, **37** (1992) 387.
28. Pandey J D, Shukla A K, Gupta S & Pandey S, *Fluid Phase Equilibria*, **103** (1995) 285.
29. Gomez-Diaz D, Mejuto J C & Navaza J M, *J Chem Eng Data*, **46** (2001) 720.
30. Diaz C, Orge B, Marino G & Tojo J, *J Chem Thermodyn*, **33(9)** (2001) 1015.
31. Resa J M, Gonzalez C, Landaluce S O & Lanz J, *J Chem Eng Data*, **47(5)** (2002) 1123.
32. Taboada M E, Veliz D M, Galleguillous H R & Graber T A, *J Chem Eng Data*, **47(5)** (2002) 1123.
33. Aznarez S, Katz M & Arancibia E L, *J Soln Chem*, **31(8)** (2002) 639.

CHAPTER - 3

Excess volume and excess isentropic compressibility of liquid mixtures

3.1 Introduction

Excess molar volume (V^E) and excess isentropic compressibility ($\beta_S{}^E$) in liquid mixtures have been used to study molecular interactions and extent of complexing, for a long time. These properties are not only useful but are easily measurable also. Mostly used methods available for the determination of these properties are measurements of density using densimeter or pyknometer, measurement of excess molar volume directly using dilatometer and theoretical methods along with the measurement of ultrasonic velocity using ultrasonic interferometer. Literature on excess molar volume (V^E) and excess isentropic compressibility ($\beta_S{}^E$) show that enormous amount of work has been done to measure these excess properties and use them to interpret molecular interactions in liquid mixtures.

Blandamer et al[1] analysed velocity data in terms of excess isentropic compressibility in alcohols + water and alkyl cyanide + water systems. However, the relation used for the calculation of excess isentropic compressibility was criticized by Bertrand et al[2]. Kiyohara et al[3] and Benson et al[4] evaluated $\beta_S{}^E$ in terms of heat capacity (C_p) data. Kiyohara et al[3] evaluated $\beta_S{}^E$ along with other properties in binary liquid mixtures comprising benzene, cyclohexane and carbon tetrachloride as components. An extensive work on V^E was carried out by Van et al[5], Cibutka et al[6] and others[7,8]. Singh et al[9] measured V^E of various ternary liquid mixtures using tri-limbed dilatometer. Pandey et al[10] evaluated V^E using Flory Statistical Theory (FST) and compared the results with experimental data. Reimann et al[11] measured V^E of alkanol + amine mixtures using densitometer and the data was used to test theoretical model. These binary combinations are very useful to study molecular interactions as amines and alcohols show strong intermolecular interactions due to hydrogen bonding. Dewan et al[12] determined V^E in pyridine + alkanol systems dilatometrically and used the results thus obtained to test Prigogine-Flory-Patterson (PFP) theory. Oswal et al[13] utilised Prigogine-Flory-Patterson theory with Lennard-Jones potential energy model to obtain relation for the estimation of β_S and utilised this relation to compute β_S of

various binary liquids having various combinations of alkanes, ethers, benzene, cyclohexane, ethyl acetate and carbon tetrachloride. Miyanaga et al[14] measured density using densimeter and computed β_S^E for binary mixtures of benzene, N,N-DMF and acetonitrile as components. Dewan et al[15] determined V^E in binary liquid mixtures of alkanols dilatometrically. Sharma et al[16] measured V^E dilatometrically for binary mixtures of ether + chloroalkanes. Nath et al[17] measured V^E of anisole + haloalkanes dilatometrically. V^E of amines + alcohols was determined by Papaioannou et al[18]. Oswal et al[19] determined V^E of ternary liquid mixtures comprising amines + cyclohexane + benzene using density measurements with the help of densitometer and utilised the data in extended Prigogine-Flory-Patterson theory.

Reddy et al[20] determined β_S^E of binary liquid mixtures comprising alcohols. Raman et al[21] determined V^E and used it to study molecular interactions in binary liquid mixtures of 2-methoxymethanol + branched alicyclic alcohols. Nath[22] utilised density, measured using pyknometer, to determine β_S^E of anisole + haloalkanes using volume fraction additivity relation for ideal isentropic compressibility (β_S^{id}). Garcia et al[23] determined V^E in binary liquid mixtures of 2-pyrrolidinone + alkanols. Pal et al[24-26] measured V^E of various alkoxyethanols + n-alkanols. V^E of acetonitrile + alcohols was measured by Aznarez et al[27]. Pal[28] determined β_S^E of butoxyethanol + water system. Aminabhavi et al[29] determined β_S^E of chloronaphthalene + monocyclic aromatics. Rao et al[30] reported β_S^E in ethyl acetate + 2-alkoxyethanols and used β_S^E to study dipolar interactions and self-association nature of mixtures. V^E of alkyl vinyl ethers + alkanes was determined by Rezanova et al[31]. Pal et al[32] determined V^E in binary liquid mixtures of alkoxyethanol + alkyl acetates. Aminabhavi et al[33] determined V^E of various binary liquid mixtures containing 1-chloronaphthalene + n-alkanes using density measurements with the help of pyknometer. Marigliano et al[34] evaluated V^E of binary systems of formamide and alkanols. Recently some more studies[35-39] on V^E and β_S^E on liquid mixtures have been carried out. Conti et al[40] measured excess enthalpies and excess heat capacities of binary and ternary liquid

mixtures comprising ethanol, N,N-dimethylformamide and cyclohexane at 298.15K. In present work, density and ultrasonic velocity of the binary and ternary liquid mixtures comprising the same components, have been determined at 308.15 K. From literature survey, it has been found that, measurements have not been carried out in these combinations at 308.15 K. N,N-DMF finds application in many chemical industries as solvent and as additive owing its complete miscibility in water and low vapour pressure. Ethanol + N,N-DMF, ethanol + cyclohexane and ethanol + N,N-DMF + cyclohexane were taken as the systems under investigation. Owing the immiscibility of N,N-DMF with cyclohexane, the measurements were carried out in miscibility range only i.e. at very low concentration of cyclohexane on N,N-DNF or vice versa for the binary N,N-DMF + cyclohexane. Density and ultrasonic data thus obtained have been utilised to evaluate excess molar volume and excess isentropic compressibility. The related parameters of β_S^E and V^E, like density (ρ), molar volume (V) and isentropic compressibility (β_S) have been computed using Flory Theory and its extended form, the validity of which have been well tested[41-45]. The necessary parameters for the pure components like thermal expansion coefficient and isothermal compressibility have been taken or calculated using the data from various sources[46-50].

3.2 Experimental

BDH (AR) and E. Merck (AR) grade chemicals were used for the measurements of ultrasonic velocity and density of binary and ternary liquid mixtures comprising ethanol, N,N-dimethylformamide and cyclohexane. Density measurements of binary and ternary liquid mixtures at varying compositions were carried out using pyknometer and ultrasonic velocity measurements for the same mixtures were carried out using ultrasonic interferometer.

Details about sample preparation, calibration and experimental techniques used has been given in chapter – 2 of this thesis.

3.3 Results and Discussion

The properties of pure liquids used as the components of binary and ternary liquid mixtures are listed in table-1. The measured values of ultrasonic velocity (u) and density (ρ) of binary and ternary liquid mixtures are listed in table-2. β_S of the mixture was evaluated using the relation

$$\beta_S = \frac{1}{u^2 \rho}$$

where, u is ultrasonic velocity and ρ is the density of the mixture.

Excess isentropic compressibility (β_S^E) values of the mixtures in various compositions were calculated using the relation:

$$\beta_s^E = \beta_s - \beta_s^{id} \qquad \ldots(1)$$

where, β_S is the isentropic compressibility of the mixture and β_S^{id} is the ideal isentropic compressibility of liquid mixtures. Since the mole fraction and volume fraction additive relations for the calculation of β_S^{id} have already been shown to be unsuitable[2], the following relation was used in the present work to evaluate β_S^{id}:

$$\beta_s^{id} = \beta_T^{id} - \frac{(\alpha^{id})^2 T V^{id}}{C_p^{id}} \qquad \ldots(2)$$

Here β_T, α, V and C_p are isothermal compressibility, thermal expansivity, molar volume and molar specific heat capacity at constant pressure, respectively. The above relation has been extensively and successfully used by various workers[14,22,33,49]. The values of V^{id}, C_p^{id}, α^{id} and β_T^{id} were calculated using the following relations:

$$V^{id} = \sum x_i V_i \qquad \ldots(3)$$

$$C_P^{id} = \sum x_i (C_P)_i \qquad \ldots(4)$$

$$\beta_T^{id} = \sum \phi_i (\beta_T)_i \qquad ...(5)$$

$$\alpha^{id} = \sum \phi_i \alpha_i \qquad ...(6)$$

Here, ϕ_i is the volume fraction of the i^{th} component of the mixture and is given by

$$\phi_i = \frac{x_i V_i}{\sum x_i V_i} \qquad ...(7)$$

The excess volume of the binary liquid was calculated using the relation:

$$V^E = V - V^{id} \qquad ...(8)$$

where, V^{id} was calculated as mole fraction average of molar volumes of pure components i.e.

$$V^{id} = \sum_{i=1}^{n} x_i V_i \qquad ...(9)$$

For comparison with experimental results, values of β_S and ρ have been also computed using the following relations, which are based upon Flory Theory and it's extended forms:

$$\text{Molar Volume}\,(V)_{Flory} = V^* \tilde{V} \qquad ...(10)$$

$$\text{Density}\,(\rho)_{Flory} = \sum x_i . M_i / V_{Flory} \qquad ...(11)$$

where, M_i is the molar mass of the i^{th} component, V^* is characteristic volume and $\tilde{V}$ is the reduced volume of the liquid mixtures. Adiabatic compressibility in terms of all Flory Theory related parameters ($\beta_{S\,Flory}$) has been evaluated as

$$(\beta_S)_{Flory} = \frac{\alpha_{Flory} T \tilde{V}}{P^*} \left(\tilde{V} - \frac{\tilde{\alpha}}{\tilde{C}_p} \right) \qquad (12)$$

where α, $\tilde{V}$, P^*, $\tilde{\alpha}$ and $\tilde{C}_p$ are thermal expansivity, reduced volume, characteristic pressure, reduced thermal expansivity and reduced specific heat capacity at constant

pressure, respectively. The required parameters for eqs (10-12), and the other necessary parameters were computed using Flory theory and its extended forms with the help of the following relations:

$$\text{Reduced volume of the i}^{\text{th}}\text{ component } (\tilde{V}_i) = \left[1 + \frac{\alpha_i T}{3(1+\alpha_i T)}\right]^3 \quad \ldots(13)$$

$$\text{Characteristic volume of the i}^{\text{th}}\text{ component } (V_i^*) = \frac{V_i}{\tilde{V}_i} \quad \ldots(14)$$

$$\text{Characteristic pressure of i}^{\text{th}}\text{ component } (P_i^*) = \frac{\alpha_i T \tilde{V}_i^2}{(\beta_T)_i} \quad \ldots(15)$$

$$\text{Reduced temperature of i}^{\text{th}}\text{ component } (\tilde{T}_i) = \frac{\tilde{V}_i^{1/3} - 1}{\tilde{V}_i^{4/3}} \quad \ldots.(16)$$

$$\text{Characteristic temperature of i}^{\text{th}}\text{ component } (T_i^*) = T/\tilde{T}_i \quad \ldots(17)$$

$$\text{Segment fraction of i}^{\text{th}}\text{ component } (\psi_i) = \frac{x_i V_i^*}{\sum x_i V_i^*} \quad \ldots(18)$$

$$\text{Site fraction of i}^{\text{th}}\text{ component } (\theta_i) = \frac{\psi_i}{\psi_i + \sum_{k \neq i} \psi_k \left(\frac{V_i^*}{V_k^*}\right)^{1/3}} \quad \ldots(19)$$

$$\text{Interaction Parameter } (x_{ij}) = P_i^* \left[1 - \left(\frac{P_j^*}{P_i^*}\right)^{1/2} \left(\frac{V_j^*}{V_i^*}\right)^{1/6}\right]^2 \quad \ldots(20)$$

$$\text{Characteristic pressure } (P^*) = \sum_i \left(\psi_i P_i^*\right) - \sum_{j \neq i} \left(\psi_i \theta_j x_{ij}\right) \quad \ldots(21)$$

$$\text{Reduced temperature } (\tilde{T}) = \frac{T}{\dfrac{P^*}{\sum \psi_i P_i^* / T_i^*}} \quad \ldots(22)$$

Ideal reduced volume $(\tilde{V}^0) = \sum_i x_i \tilde{V}_i$...(23)

Ideal reduced temperature $(\tilde{T}^0) = \frac{\tilde{V}^{0^{1/3}} - 1}{\tilde{V}^{0^{4/3}}}$...(24)

Thermal expansivity $(\alpha) = \frac{3(\tilde{V}^{1/3} - 1)}{T(1 - 3(\tilde{V}^{1/3} - 1)}$...(25)

Reduced thermal expansivity $(\tilde{\alpha}) = \alpha T^*$...(26)

Reduced specific heat capacity at constant pressure

$$(\tilde{C}_p) = \frac{C_P}{P^* V^* / T^*} \quad \text{...(27)}$$

Excess specific heat capacity

$$(C_p^E) = \frac{P^* V^*}{T^*} \left[\frac{1}{\left(\frac{4}{3} \tilde{V}^{-1/3} - 1 \right)} - \sum_i \left(\frac{x_i}{\frac{4}{3} \tilde{V}_i^{-1/3} - 1} \right) \right] \quad \text{...(28)}$$

Specific heat capacity at constant pressure

$$(C_p)_{Flory} = (C_P^E)_{Flory} + C_P^{id} \quad \text{...(29)}$$

Excess reduced volume $(\tilde{V}^E) = \tilde{V}^{0^{7/3}} \left(\frac{4}{3} - \tilde{V}^{0^{1/3}} \right)^{-1} \left(\tilde{T} - \tilde{T}^0 \right)$...(30)

Excess molar volume $V^{E}{}_{Flory} = \sum_i x_i V_i^* \tilde{V}^E$...(31)

Reduced Volume $(\tilde{V}) = \tilde{V}^E + \tilde{V}^0$...(32)

The experimental values of β_S and ρ have been compared with the calculated values (using eqs 10-12) and the results have been depicted in table-2. The good agreement between the experimental and calculated values has been obtained. Table-2

and ternary liquid mixtures. The β_S^E and V^E values for the systems under consideration are graphically represented in Fig. 1-6.

The values of excess molar volume and excess molar compressibility of binary liquid mixture ethanol + N,N-DMF are negative in whole composition range, showing a strong interaction between ethanol and N,N-DMF. These results are quite obvious as N,N-DMF orient themselves randomly in pure state[14]. But with ethanol molecules, they form more ordered arrangements due to the hydrogen bonding between N...H-O. These excess properties are found to be low positive in the case of ethanol + cyclohexane. This shows the weak interaction between ethanol and cyclohexane. This might be due to structure breaking interaction of orderly arranged (hydrogen bonded) molecules of ethanol, by cyclohexane. Owing the immiscibility of N,N-DMF with cyclohexane, the measurements were carried out in miscibility range only i.e. at very low concentration of cyclohexane on ethanol or vice versa. Here, low negative values of β_S^E and V^E are observed at higher N,N-DMF concentrations. In case of ternary liquid mixture of ethanol + N,N-DMF + cyclohexane, both excess properties change from negative to positive by the addition of cyclohexane. This may be due to the disruption of hard arrangement of binary liquid mixture of ethanol + N,N-DMF, by the addition of cyclohexane. Along with the study of the molecular interactions, the applicability of Flory Theory for the evaluation of β_S and ρ in the case, when only easily measurable experimental data are available, has also been authenticated by the present study.

3.4 References

1. Blandamer M J & Waddington D, *J Phys Chem*, **74(12)** (1970) 2569.
2. Bertrand G L & Smith L E, *J Phys Chem*, **74(23)** (1970) 4171.
3. Kiyohara O, Halpin C J & Benson G C, *J Chem Thermodyn*, **10** (1978) 721.
4. Benson G C, Kiyohara O, *J Chem Thermodyn*, **11** (1979) 1061.
5. Van V T & Patterson D, *J Soln Chem*, **11** (1982) 793.
6. Cibutka I, Erving M B & Mcglashan, *J Chem Thermodyn*, **15** (1983) 49.

and ternary liquid mixtures. The β_S^E and V^E values for the systems under consideration are graphically represented in Fig. 1-6.

The values of excess molar volume and excess molar compressibility of binary liquid mixture ethanol + N,N-DMF are negative in whole composition range, showing a strong interaction between ethanol and N,N-DMF. These results are quite obvious as N,N-DMF orient themselves randomly in pure state[14]. But with ethanol molecules, they form more ordered arrangements due to the hydrogen bonding between N...H-O. These excess properties are found to be low positive in the case of ethanol + cyclohexane. This shows the weak interaction between ethanol and cyclohexane. This might be due to structure breaking interaction of orderly arranged (hydrogen bonded) molecules of ethanol, by cyclohexane. Owing the immiscibility of N,N-DMF with cyclohexane, the measurements were carried out in miscibility range only i.e. at very low concentration of cyclohexane on ethanol or vice versa. Here, low negative values of β_S^E and V^E are observed at higher N,N-DMF concentrations. In case of ternary liquid mixture of ethanol + N,N-DMF + cyclohexane, both excess properties change from negative to positive by the addition of cyclohexane. This may be due to the disruption of hard arrangement of binary liquid mixture of ethanol + N,N-DMF, by the addition of cyclohexane. Along with the study of the molecular interactions, the applicability of Flory Theory for the evaluation of β_S and ρ in the case, when only easily measurable experimental data are available, has also been authenticated by the present study.

3.4 References

1. Blandamer M J & Waddington D, *J Phys Chem*, **74(12)** (1970) 2569.
2. Bertrand G L & Smith L E, *J Phys Chem*, **74(23)** (1970) 4171.
3. Kiyohara O, Halpin C J & Benson G C, *J Chem Thermodyn*, **10** (1978) 721.
4. Benson G C, Kiyohara O, *J Chem Thermodyn*, **11** (1979) 1061.
5. Van V T & Patterson D, *J Soln Chem*, **11** (1982) 793.
6. Cibutka I, Erving M B & Mcglashan, *J Chem Thermodyn*, **15** (1983) 49.

7. Luo B, Harnam S E M & Benson G C, *J Chem Thermodyn*, **18** (1986) 1043.
8. Zhang D & Benson G C, *J Chem Thermodyn*, **18** (1986) 697.
9. Singh P P & Sharma S P, *J Chem Eng Data*, **30** (1985) 477.
10. Pandey J D, Shukla R K, Shukla A K & Rai R D, *J Chem Soc Farad Trans,* **84** (1988) 1853.
11. Reimann R & Heintz A, *J Soln Chem*, **20** (1991) 29.
12. Dewan R K, Mehta S K, Parashar R & Bala K, *J Chem Soc Farad Trans,* **87(10)** (1991) 1561.
13. Oswal S L, Dave J P & Managoli V, *Acoustics Letters,* **16(6)** (1992) 143.
14. Miyanaga S, Tamura K & Murakami S, *J Chem Thermodyn*, **24** (1992) 1077.
15. Dewan R K, Mehta S K, Parashar R & Kaur H, *J Chem Soc Farad Trans,* **88** (1992) 227.
16. Sharma S C, Joshi I M, Singh J & Gupta A, *J Soln Chem*, **21** (1992) 289.
17. Nath J & Chaudhary S K, *J Chem Eng Data*, **37** (1992) 387.
18. Papaioannou D, Bvidakes M & Panayiotou C G, *J Chem Eng Data*, **38** (1993) 370.
19. Oswal S L & Patel S G, *J Chem Soc Farad Trans,* **90(8)** (1994) 1083.
20. Reddy V K, Rambabu K, Devarajulu T & Krishnaiah A, *J Chem Eng Data*, **40** (1995) 124.
21. Raman G K, Vanketeswarlu P, Rambabu K & Krishnan K M, *J Chem Eng Data*, **40** (1995) 128.
22. Nath J, *J Chem Thermodyn*, **28** (1996) 481.
23. Garcia B, Hoyuelos F J, Alcalde R & Leal J M, *Can J Chem*, **74** (1996) 121.
24. Pal A & Kumar A, *Acoustics Letters*, **20** (1997) 203.
25. Pal A & Kumar A, *Acoustics Letters*, **22** (1999) 168.
26. Pal A & Dass G, *J Soln Chem*, **28** (1999) 237.
27. Aznarez S B & Postigo M A, *J Soln Chem*, **27** (1998) 1045.
28. Pal A, *Ind J Chem*, **37A** (1998) 109.
29. Aminabhavi T M, Banerjee K & Balundgi R H, *Ind J Chem*, **38A** (1999) 768.

30. Rao M V P, Chandershekhar G & Vankatesu P, *J Chem Eng Data*, **45** (2000) 590.

31. Rezanova E N, Leppla C, Lichtenthanler R N, *J Chem Thermodyn*, **45** (2000) 1019.

32. Pal A & Bhardwaj R K, *J Ind Chem Soc*, **78** (2001) 18.

33 Aminabhavi T M & Banerjee K, *Ind J Chem*, **40A** (2001) 53.

34. Marigliano A C G & Solimo H N, *J Chem Eng Data*, **47(4)** (2002) 769.

35. Diaz C, Org B, Marino G & Tojo J, *J Chem Thermodyn*, **33(9)** (2001) 1015.

36. Pal A & Bhardwaj R K, *J Chem Thermodyn*, **34(8)** (2002) 1157.

37. Naejus R, Damas C, Lemordant D, Coudert R & Willmann P, *J Chem Thermodyn*, **34(6)** (2002) 795.

38. Pal A & Bhardwaj R K, *J Chem Eng Data*, **47(5)** (2002) 1128.

39. Peleteiro J, Gonzalez D, Cerdeirina C A & Romani L, *J Chem Thermodyn*, **34(4)** (2002) 485.

40. Conti G, Gianni P, Lepori L & Matteoli E, *Fluid Phase Equilibria*, **105** (1995) 93.

41. Flory P J, *J Amer Chem Soc*, **87:9** (1965) 1833.

42. Abe A & Flory P J, *J Amer Chem Soc*, **87:9** (1965) 1838.

43. Islam M R & Quadri S K, *Acoustics Letters*, **11(2)** (1988) 237.

44. Oswal S L, *Acoustics Letters*, **14(1)** (1990) 17.

45. Pandey J D & Sanguri V, *J Chem Research (S)*, (2001) 344.

46. Partington J R, *An Advance Treatise on Physical Chem*, Vol.2, 1950.

47. *CRC Handbook of Chemistry and Physics,* CRC Press, Boca Raton, New York, 1979-80.

48. Reid R C, Prausnitz J M & Poling B E, *The Properties of Gases and Liquids*, McGraw-Hill Inc, 4th Ed, 1987.

49. Hu J, Tamura K & Murakami S, *Fluid Phase Equilibria*, **134** (1997) 239.

50. Sastry N V, Patel M C & Patel S R, *Fluid Phase Equilibria*, **155** (1999) 261.

Table-1

Properties of pure compounds at 308.15 K

Compounds	ρ_{expt} kg m^{-3}	u_{expt} m s^{-1}	n_{expt}	V m^{-3} mol^{-1}	α 10^{-3} K^{-1}	β_T 10^{-11} m^2 N^{-1}	β_S 10^{-11} m^2 N^{-1}	Cp J mol^{-1} K^{-1}
Ethanol	777.9	1117.46	1.357	59.22	1.125	123.21	102.95	114.0
N,N-Dimethylformamide	935.5	1432.00	1.423	78.13	0.879	64.34	52.13	152.4
Cyclohexane	764.2	1209.14	1.420	110.13	1.246	122.45	89.50	159.9

Table-2

Experimental and calculated values of density (ρ) and isentropic compressibility (β_S) and excess properties (V^E & β_S^E) in liquid mixtures at 308.15 K

2. a) Binary Liquid Mixture: Ethanol (1) + N,N-dimethylformamide (N,N-DMF) (2)

X_1	x_2	u_{expt}	ρ (kg m^{-3})			β_s (10^{-11} m^2 N^{-1})			$\beta_s^E{}_{expt}$	$V^E{}_{expt}$
		m s^{-1}	*Expt.*	*Calc.*	*% Diff*	*Expt.*	*Calc.*	*% Diff*	10^{-11} m^2 N^{-1}	10^{-6} m^3 mol^{-1}
0.0000	1.0000	1432.00	935.5	935.5	-	52.13	52.13	-	0.00	0.00
0.0506	0.9494	1417.14	930.5	929.4	0.12	53.51	53.47	0.07	-0.64	-0.09
0.1261	0.8739	1401.57	922.8	920.1	0.29	55.16	55.59	(0.78)	-2.08	-0.24
0.2018	0.7982	1386.00	914.7	910.5	0.46	56.91	57.91	(1.76)	-3.54	-0.37
0.3613	0.6387	1349.14	893.4	888.7	0.53	61.50	63.51	(3.27)	-6.11	-0.42
0.5009	0.4991	1306.29	873.1	867.9	0.60	67.12	69.40	(3.40)	-7.23	-0.45
0.6623	0.3377	1256.00	846.7	841.8	0.58	74.87	77.70	(3.78)	-7.90	-0.42
0.8281	0.1719	1199.43	816.2	812.1	0.50	85.16	88.46	(3.88)	-7.05	-0.33
0.9032	0.0969	1167.29	801.2	797.6	0.45	91.60	94.30	(2.95)	-5.17	-0.28
0.9782	0.0218	1135.14	784.7	782.5	0.28	98.90	100.88	(2.00)	-2.63	-0.17
1.0000	0.0000	1117.46	777.9	777.9	-	102.95	102.95	-	0.00	0.00
		APD (with signs included):			**0.35**			**(1.98)**		

2.b) Binary Liquid Mixture: Ethanol (1) + Cyclohexane (2)

x_1	x_2	u_{expt}	ρ (kg m^{-3})			β_s (10^{-11} m^2 N^{-1})			$\beta_s^E{}_{expt}$	$V^E{}_{expt}$
		m s^{-1}	*Expt.*	*Calc.*	*% Diff*	*Expt.*	*Calc.*	*% Diff*	10^{-11} m^2 N^{-1}	10^{-6} m^3 mol^{-1}
0.0000	1.0000	1209.14	764.2	764.2	-	89.50	89.50	-	0.000	0.000
0.0542	0.9458	1200.29	764.2	764.3	(0.01)	90.83	90.34	0.54	0.800	0.059
0.1278	0.8722	1188.57	764.2	764.5	(0.04)	92.63	91.50	1.22	1.850	0.136
0.2027	0.7973	1179.14	764.3	764.8	(0.07)	94.10	92.70	1.49	2.530	0.199
0.3648	0.6352	1160.29	764.9	765.6	(0.09)	97.11	95.37	1.79	3.690	0.302
0.5004	0.4996	1148.57	766.2	766.7	(0.07)	98.93	97.60	1.34	3.810	0.305
0.6640	0.3360	1134.29	768.4	768.8	(0.05)	101.15	100.13	1.01	3.770	0.284
0.8315	0.1685	1121.43	772.7	772.2	0.06	102.91	102.20	0.69	2.930	0.132
0.9034	0.0966	1120.29	775.2	774.3	0.12	102.78	102.75	0.03	1.580	0.042
0.9763	0.0237	1118.29	777.8	776.9	0.12	102.81	102.97	(0.16)	0.300	-0.037
1.0000	0.0000	1117.46	777.9	777.9	-	102.95	102.95	-	0.000	0.000
		APD (with signs included):			**(0.01)**			**0.72**		

2.c) Binary Liquid Mixture: N,N-dimethylformamide (1) + Cyclohexane (2) [Only in miscibility range]

x_1	x_2	u_{expt}	ρ (kg m^{-3})			β_s (10^{-11} m^2 N^{-1})			$\beta_s^E{}_{expt}$	$V^E{}_{expt}$
		m s^{-1}	*Expt.*	*Calc.*	*% Diff*	*Expt.*	*Calc.*	*% Diff*	10^{-11} m^2 N^{-1}	10^{-6} m^3 mol^{-1}
0.0000	1.0000	1209.14	764.2	764.2	-	89.50	89.50	-	89.500	0.000
0.0293	0.9707	1209.43	766.3	768.1	(0.23)	89.22	88.31	1.02	89.220	0.208
0.0402	0.9598	1210.29	767.3	769.6	(0.30)	88.97	87.86	1.25	88.970	0.256
0.0548	0.9452	1210.57	768.8	771.5	(0.35)	88.76	87.27	1.68	88.760	0.304
0.8443	0.1557	1381.43	902.1	902.3	(0.02)	58.09	57.44	1.12	58.090	-0.182
0.9001	0.0999	1391.43	913.5	913.9	(0.04)	56.54	55.51	1.82	56.540	-0.107
0.9592	0.0408	1406.00	926.0	926.5	(0.05)	54.63	53.50	2.07	54.630	-0.016
1.0000	0.0000	1432.00	935.5	935.5	-	52.13	52.13	-	52.130	0.000
		APD (with signs included):			**(0.13)**			**1.12**		

2. d) Ternary Liquid Mixture: Ethanol (1) + N,N-DMF (2) + Cyclohexane (3)

x_1	x_2	x_3	u_{expt}	ρ (kg m^{-3})			β_s (10^{-11} m^2 N^{-1})			$\beta_s^E{}_{expt}$	$V^E{}_{expt}$
			m s^{-1}	*Expt.*	*Calc.*	*% Diff*	*Expt.*	*Calc.*	*% Diff*	10^{-11} m^2 N^{-1}	10^{-6} m^3 mol^{-1}
0.4675	0.4682	0.0643	1285.43	860.9	858.2	0.31	70.30	71.20	(1.28)	-6.000	-0.297
0.4305	0.4314	0.1381	1264.29	847.9	847.5	0.05	73.78	73.21	0.77	-4.560	-0.120
0.3940	0.3949	0.2111	1249.43	834.9	837.7	(0.34)	76.73	75.09	2.14	-3.370	0.155
0.3071	0.3076	0.3853	1222.29	813.3	817.0	(0.45)	82.30	79.14	3.84	-1.180	0.258
0.2416	0.2420	0.5164	1203.43	797.8	803.4	(0.70)	86.55	81.82	5.47	1.140	0.514
0.2056	0.2059	0.5885	1197.71	789.4	796.5	(0.90)	88.31	83.18	5.81	2.020	0.726
0.1451	0.1455	0.7094	1195.14	779.2	785.9	(0.86)	89.85	85.27	5.10	2.330	0.763
0.1232	0.1234	0.7534	1194.86	776.2	782.3	(0.79)	90.24	85.98	4.72	2.340	0.709
0.0703	0.0704	0.8593	1195.43	769.1	774.1	(0.65)	90.98	87.58	3.74	2.290	0.632
			APD (with signs included):			**(0.48)**			**3.37**		

Fig. 1-6: Excess properties (V^E and $\beta_S{}^E$) in liquid mixtures

Fig. 1: Ethanol (1) + N,N-DMF (2)

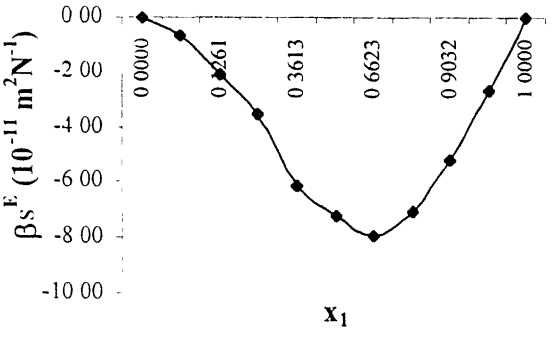


Fig. 2: Ethanol (1) + N,N-DMF (2)

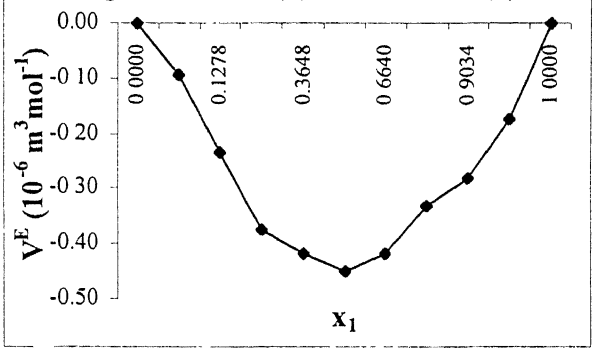


Fig. 3: Ethanol (1)+Cyclohexane(2)

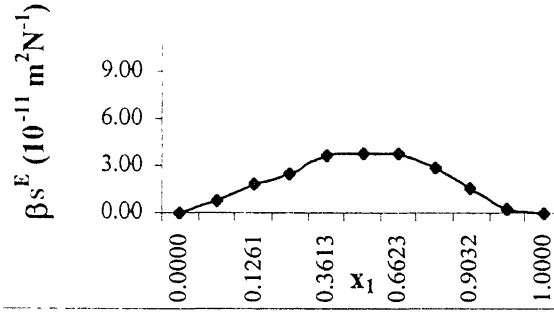


Fig. 4: Ethanol (1)+Cyclohexane(2)

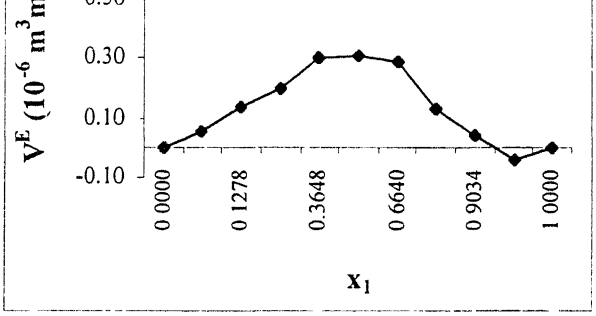


Fig. 5: Ethanol (1) + N,N-DMF(2) + Cyclohexane(3)

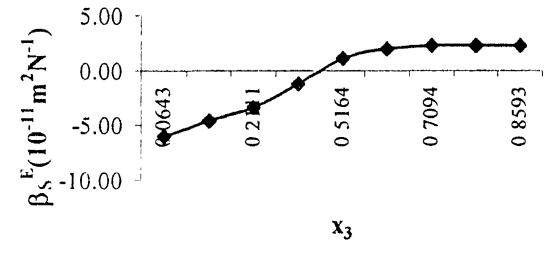
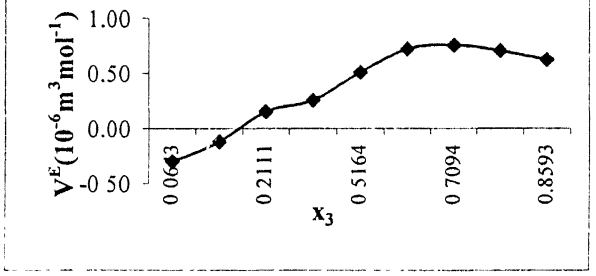


Fig.6: Ethanol (1) + Cyclohexane (2) + Cyclohexane (3)



CHAPTER – 4

Ultrasonic and refractometric studies of liquid mixtures

4.1 Introduction

Propagation of ultrasonic waves through a medium is one of the important physico-chemical properties of a system. The sound waves having a frequency of 1.4 KHz to 800 MHz, called ultrasonic waves, have been extensively used in chemical industries, medicine, cavitating the fluids and many engineering works. Ultrasonic studies in liquids and liquid mixtures have been the subjects of enormous interest during last three decades, not only to study the molecular interactions in the liquids but also to evaluate various interesting parameters. Refractive index is another important physical property of a liquid and liquid mixtures, which can be used to study molecular interactions and to evaluate other important parameters. Refractive index of a liquid is the ratio of the speed of light in vacuum to that in liquid. For a given wavelength of light, refractive index depends on nature of liquid, pressure and temperature. Literature survey shows that enormous amount of work has been done to measure or evaluate the refractive index and ultrasonic velocity of liquids and liquid mixtures.

Various relations and mixing rules relating ultrasonic velocity and refractive index with other parameters of the liquids are given by various workers[1-19]. Ultrasonic and refractometric studies have gained enormous attention for long time. Reese et al[20] measured ultrasonic velocity in various liquids. Mishra et al[21] evaluated ultrasonic velocity using Collision Factor Theory and Free Length Theory. It has been shown by the workers that these both theories are approximate in nature. Aminabhavi et al[22] utilised various mixing rules for the evaluation of refractive index to test for their validity. Pandey and Mishra[23] evaluated ultrasonic velocity in various organic liquids using the Carnahan-Starling rigid sphere equation of state. Pandey et al[24] evaluated ultrasonic velocity using Flory theory in conjunction with Auerbach[4] empirical relation. Islam et al[25] determined ultrasonic velocity in aniline + alcohols. These workers also evaluated ultrasonic velocity using Flory theory in conjunction with Auerbach[4] empirical relation. Oswal et al[26] determined ultrasonic velocity and refractive index for binary liquid mixtures comprising ethyl acetate, benzene and

cyclohexane at various temperatures. The values were employed to evaluate other molecular parameters. Narayana et al[27] studied ultrasonic velocity in liquid perfluoropentanes (Flutec PP50). Oswal[28] evaluated ultrasonic velocity on the basis of Prigigine-Flory-Patterson (PFP) theory, in binary liquid mixtures comprising alkanes, benzene, carbon tetrachloride and cyclohexane as components. Khanwalker et al[29] developed a model to evaluate ultrasonic velocity using Flory theory. Nakai et al[30] determined ultrasonic velocity in various ether + hydrocarbon mixtures. Dhanalakshmi et al[31] determined ultrasonic velocity in carbohydrate solutions. Aralaguppi et al[32] carried out studies on refractive index and ultrasonic velocity in diglyme + ester mixtures. Pandey et al[33] measured ultrasonic velocity and refractive index in two ternary liquid mixtures comprising cyclohexane, toluene and carbon tetrachloride as components. The workers modified Bertrand-Acree approach. Aminabhavi et al[34] determined refractive index and ultrasonic velocity in diglyme + esters. The mixing rules for refractive index were also tested for the systems under investigation. Pal et al[35] determined ultrasonic velocity in alkoxyalkanol + water systems. Hu et al[36] measured ultrasonic velocity of various binary liquids including ethyl acetate, benzene, ethanol & fluoroalkanol. Sastry et al[37] measured ultrasonic velocity and density of liquids and compared the results with the values obtained from Collision Factor Theory and Free Length Theory. Refractive index and ultrasonic velocity are finding equal interest in the recent past also. Pal et al[38] measured ultrasonic velocity of various diglyme + esters and utilised them to study molecular interactions. Lee et al[39] measured refractive index in $LiBr+H_2O+1,3$-propanediol system. Rodriguez et al[40] determined ultrasonic velocity and refractive index in ternary liquid mixtures of alkyl carbonates + methanol + toluene. Gomez-Diaz et al[41] measured refractive index in 2,2,4-trimethylpentane. Diaz et al[42] measured refractive index and ultrasonic velocity in cyclohexane + n-heptane + aromatic hydrocarbons. Nayak et al[43] determined ultrasonic velocity and refractive index in ethyl chloroacetate + aromatic liquids. Rosa et al[44] determined ultrasonic velocity of binary liquid mixtures comprising methanol and esters. Ultrasonic velocity in high molecular weight paraffins has been measured by Dutor et al[45]. Pal

and Bhardwaj[46] measured ultrasonic velocity in alkoxyalkanols + toluene systems. Comeli et al[47] measured refractive index of binary liquid mixtures containing alcohols and ethers. Gomez-Diaz et al[48] measured refractive index of ternary liquid mixture comprising alkanes and cyclohexane.

In the present work, refractive index and ultrasonic velocity of the binary and ternary liquid mixtures, comprising ethanol, N,N-dimethylformamide (N,N-DMF) and cyclohexane as components, have been determined at 308.15K. Ethanol + N,N-DMF, ethanol + cyclohexane and ethanol + N,N-DMF + cyclohexane were taken as the systems under investigation. Owing the immiscibility of N,N-DMF with cyclohexane in certain concentrations, the measurements were carried out in miscibility range only i.e. at very low concentration of cyclohexane on N,N-DMF or vice versa for the binary liquid mixture of N,N-DMF + cyclohexane. From literature survey, it has been found that these measurements have not been carried out in these combinations at 308.15K. Various additive rules and Flory Statistical Theory have also been employed to evaluate these properties for the same composition. For the evaluation of ultrasonic velocity using Flory statistical theory, an approach different than the approaches employed by most of the previous workers, has been used. The calculated values have been compared against the measured values to test the validity and relative merits of these rules or relations. Deviations in molar sound velocity (ΔR) and molar refractivity (ΔR_m) from volume fraction average values have also been evaluated. These deviations have been employed to interpret the nature of molecular interactions in binary and ternary liquid mixtures under study. Ultrasonic velocity values of the liquid mixtures of given composition have also been computed using Flory theory and its extended form, the details about which has already been given in chapter-3 of this thesis.

4.2 Experimental

BDH (AR) and E. Merck (AR) grade chemicals were used for the measurements of ultrasonic velocity and refractive index of binary and ternary liquid mixtures

comprising ethanol, N,N-DMF and cyclohexane. Refractive index measurements of binary and ternary liquid mixtures at varying compositions were carried out using Abbe Refractometer and ultrasonic velocity measurements for the same mixtures were carried out using Ultrasonic Interferometer. Details about the purification of the chemicals, solution preparation and experimental techniques utilised have been given in chapter-2 of this thesis.

4.3 Theoretical

Ultrasonic velocity and refractive index are very useful and easily measurable properties of the liquids and liquid mixtures. These properties are useful not only to study the nature of liquids and liquid mixtures but they can also be used to deduce the important parameters of the liquid systems. Some important relations of ultrasonic velocity and refractive index of liquids and liquid mixtures are discussed here.

A) Various relations related to ultrasonic velocity of liquids and liquid mixtures

a) **Thermodynamic Relation:** Ultrasonic velocity (u) is related with isentropic compressibility (β_S) and density (ρ) of the liquids and liquid mixtures as:

$$u = \left(\frac{1}{\beta_s \rho}\right)^{1/2} \qquad ...(1)$$

where

$\beta_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$ and the term $\left(\frac{\partial V}{\partial P}\right)_S$ is related with other parameters through th thermodynamic relation

$$\left(\frac{\partial V}{\partial P}\right)_S = \left(\frac{\partial V}{\partial P}\right)_T + \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P^2 .$$

b) **Relation with molar sound velocity and molar compressibility:** Molar sound velocity[3] (R) and molar compressibility[5] (W) of liquids and liquid mixtures are related with ultrasonic velocity as:

comprising ethanol, N,N-DMF and cyclohexane. Refractive index measurements of binary and ternary liquid mixtures at varying compositions were carried out using Abbe Refractometer and ultrasonic velocity measurements for the same mixtures were carried out using Ultrasonic Interferometer. Details about the purification of the chemicals, solution preparation and experimental techniques utilised have been given in chapter-2 of this thesis.

4.3 Theoretical

Ultrasonic velocity and refractive index are very useful and easily measurable properties of the liquids and liquid mixtures. These properties are useful not only to study the nature of liquids and liquid mixtures but they can also be used to deduce the important parameters of the liquid systems. Some important relations of ultrasonic velocity and refractive index of liquids and liquid mixtures are discussed here.

A) Various relations related to ultrasonic velocity of liquids and liquid mixtures

a) **Thermodynamic Relation:** Ultrasonic velocity (u) is related with isentropic compressibility (β_S) and density (ρ) of the liquids and liquid mixtures as:

$$u = \left(\frac{1}{\beta_s \rho}\right)^{1/2} \qquad \ldots(1)$$

where

$\beta_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$ and the term $\left(\frac{\partial V}{\partial P}\right)_S$ is related with other parameters through the thermodynamic relation

$$\left(\frac{\partial V}{\partial P}\right)_S = \left(\frac{\partial V}{\partial P}\right)_T + \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P^2 .$$

b) **Relation with molar sound velocity and molar compressibility:** Molar sound velocity[3] (R) and molar compressibility[5] (W) of liquids and liquid mixtures are related with ultrasonic velocity as:

$$R = \frac{M}{\rho} u^{1/3} \qquad \ldots(2)$$

and

$$W = \frac{M}{\rho} \beta_S^{-1/7} \qquad \ldots(3)$$

where, M is molar mass and for a binary liquid mixture at given composition, it is given by $M_{mix}=\Sigma x_i M_i$.

c) **Van Dael and Vangeel Relation (VD):** Van Dael and Vangeel[11] proposed the following relation for the evaluation of ultrasonic velocity of liquid mixture from the knowledge of ultrasonic velocity of pure components (u_i):

$$\frac{1}{\sum (x_i M_i)} \frac{1}{u_{mix}^2} = \sum \left(\frac{x_i}{u_i^2 M_i} \right) \qquad \ldots(4)$$

d) **Nomoto Relation (NR):** On assumption that, molar sound velocity and molar volume (V) are mole fraction additive, Nomoto[8] proposed the following relation for the evaluation of ultrasonic velocity of liquid mixture from the knowledge of molar sound velocity of i^{th} component of the mixture (R_i):

$$u_{mix} = \left(\frac{R_{mix}}{V_{mix}} \right)^3 = \left(\frac{\sum x_i R_i}{\sum x_i V_i} \right)^3 \qquad \ldots(5)$$

The molar sound velocity of i^{th} component can be evaluated as:

$$R_i = \frac{M_i}{\rho_i} u_i^{1/3},$$

where M and ρ are molar mass and density of pure liquids.

e) **Junjie's Relation (JR):** Junjie[12] proposed the following relation for the evaluation of the ultrasonic velocity of the liquid mixtures:

$$u_{mix} = \left(\sum x_i V_i \right) \Big/ \left[\left(\sum x_i M_i \right)^{1/2} \left(\sum \frac{x_i V_i}{\rho_i u_i^2} \right)^{1/2} \right] \qquad \ldots(6)$$

f) **Collision Factor Theory (CFT):** Schaaffs[2] on the basis of Collision Factor Theory proposed the following relation for the evaluation of ultrasonic velocity:

$$u = u_{\infty} S B / \mathrm{r} \qquad ...(7)$$

where, S is collision factor, U_{∞}=1600 ms^{-1} and B is geometrical volume, which can be computed from molecular radius (r) as:

$$B = \frac{4}{3} \pi N r^3 \qquad ...(8)$$

The molecular radius required for eq (8), can be evaluated using the relation

$$r = \left(\frac{3b}{16 \pi \mathrm{N}} \right)^{1/3} \qquad ...(9)$$

where, b can be evaluated using the following relation:

$$b = \left(\frac{M}{\rho} \right) - \frac{RT}{\rho u^2} \left(\left(1 + \frac{Mu^2}{3RT} \right)^{1/2} - 1 \right) \qquad ...(10)$$

The eqs (7) and (8) can be employed to evaluate S_i and B_i for components of liquid mixtures and the ultrasonic velocity of the liquid mixture can be evaluated using the relation

$$u_{mix} = u_{\infty} \left(\sum x_i S_i \right) \left(\sum x_i B_i \right) \Big/ V \qquad ...(11)$$

g) **Ultrasonic velocity based upon relations of Flory Statistical Theory (FST):** Ultrasonic velocity has been deduced using Flory theory with its extended form by several workers[24,25,28,29]. These deductions are either based upon evaluation of ultrasonic velocity using Flory theory in conjunction with Auerbach[4] empirical relation or using specific volume obtained from Flory theory. In present work, the following relation has been used for the evaluation of ultrasonic velocity of liquid mixtures, which uses the parameters purely deduced from Statistical Theory. The aim of employing this relation is that it uses all the interaction parameter X_{ij} and

provides good method for the evaluation of various parameters of binary and ternary liquid mixtures.

$$u_{Flory} = \left[\beta_{S\,Flory} \frac{\sum x_i M_i}{V_{Flory}} \right]^{-1/2} \qquad ...(12)$$

and

$$V_{Flory} = V^* \tilde{V}$$

where, V * and $\tilde{V}$ are characteristic and reduced volumes respectively.

The related parameters required for eq (12) can be evaluated from various relations based upon Flory Statistical Theory, detail of which has been already given in chapter-3 of this thesis.

h) Deviation in molar sound velocity from ideal values (ΔR): Volume fraction additivity relation for the evaluation of the ideal molar sound velocity (R^{id}), has been shown to be suitable by previous workers[32,34]. Same relation has been used in the present study also. But instead of the relation

$$\Delta R = (R)_{mix} - R^{id}$$

the following relation has been utilised for the convenience in the interpretation of molecular interaction:

$$\Delta R = R^{id} - (R)_{mix}$$

or

$$\Delta R = \sum(\phi_i R_i) - (R)_{mix} \qquad ...(13)$$

where, R_i and ϕ_i are molar sound velocity and mole fraction of pure components.

B) Various Relations related to refractive index of liquid mixtures

a) **Molar Refractivity (R_m):** Using refractive index of liquid mixture (n) at a given composition and its molar volume (V), molar refractivity can be deduced using the relation

$$R_m = \frac{(n^2 - 1)}{(n^2 + 2)} V \qquad ...(14)$$

The molar refractivity data can be utilised to evaluate the deviations in molar refractivity from volume fraction average (ΔR_m), which gives insight of the molecular interactions and mixing phenomenon in liquid mixtures. Deviations in molar refractivity (ΔR_m) can be evaluated in two forms:

i) Theoretical deviation of molar refractivity from ideal molar refractivity, $(\Delta R_m)_{theo}$: To evaluate $(\Delta R_m)_{theo}$, molar refractivity (R_m) is computed using theoretically using mixing rules. $(\Delta R_m)_{theo}$ then is computed using the relation

$$(\Delta R_m)_{theo} = \sum \phi_i (R_m)_i - (R_m)_{theo} \qquad ...(15)$$

where $(R_m)_i$ and ϕ_i are molar refractivity and volume fractions of components of the liquid mixtures.

ii) Experimental deviation of molar refractivity from ideal molar refractivity, $(\Delta R_m)_{expt}$: To evaluate $(\Delta R_m)_{expt}$, molar refractivity $(R_m)_{expt}$ is computed using eq (14) taking refractive index and molar volume of the liquid mixture of the concern. From the knowledge of $(R_m)_{expt}$, $(\Delta R_m)_{expt}$ can be evaluated as:

$$(\Delta R_m)_{expt} = \sum \phi_i (R_m)_i - (R_m)_{expt} \qquad ...(16)$$

b) **Mixing rules for the evaluation of refractive index of liquid mixtures:** Using density or molar volume and the refractive index of pure components, refractive index of liquid mixture (n) at a given composition can be predicted using some mixing rules. These values of theoretical refractive index of mixture can in turn

B) Various Relations related to refractive index of liquid mixtures

a) **Molar Refractivity (R_m):** Using refractive index of liquid mixture (n) at a given composition and its molar volume (V), molar refractivity can be deduced using the relation

$$R_m = \frac{(n^2 - 1)}{(n^2 + 2)} V \qquad ...(14)$$

The molar refractivity data can be utilised to evaluate the deviations in molar refractivity from volume fraction average (ΔR_m), which gives insight of the molecular interactions and mixing phenomenon in liquid mixtures. Deviations in molar refractivity (ΔR_m) can be evaluated in two forms:

i) Theoretical deviation of molar refractivity from ideal molar refractivity, $(\Delta R_m)_{theo}$: To evaluate $(\Delta R_m)_{theo}$, molar refractivity (R_m) is computed using theoretically using mixing rules. $(\Delta R_m)_{theo}$ then is computed using the relation

$$(\Delta R_m)_{theo} = \sum \phi_i (R_m)_i - (R_m)_{theo} \qquad ...(15)$$

where $(R_m)_i$ and ϕ_i are molar refractivity and volume fractions of components of the liquid mixtures.

ii) Experimental deviation of molar refractivity from ideal molar refractivity, $(\Delta R_m)_{expt}$: To evaluate $(\Delta R_m)_{expt}$, molar refractivity $(R_m)_{expt}$ is computed using eq (14) taking refractive index and molar volume of the liquid mixture of the concern. From the knowledge of $(R_m)_{expt}$, $(\Delta R_m)_{expt}$ can be evaluated as:

$$(\Delta R_m)_{expt} = \sum \phi_i (R_m)_i - (R_m)_{expt} \qquad ...(16)$$

b) **Mixing rules for the evaluation of refractive index of liquid mixtures:** Using density or molar volume and the refractive index of pure components, refractive index of liquid mixture (n) at a given composition can be predicted using some mixing rules. These values of theoretical refractive index of mixture can in turn

be used to evaluate theoretical values of molar refractivity and then theoretical deviations in refractive index using eq (15). Some important mixing rules are discussed here.

Dale-Gladstone relation (D-G): Based upon strict volume additivity assumption, Dale et al[16] proposed the mixing rule, which is given by

$$\left[\frac{n-1}{\rho}\right] = \sum\left(\frac{n_i - 1}{\rho_i} W_i\right) \qquad ...(17)$$

where n and ρ are refractive index and density of liquid mixture, and n_i and W_i are the refractive index and weight fraction of i^{th} component of the mixture. Since, weight fraction and volume fraction (ϕ_i) are related with the relation

$$W_i = \frac{\phi_i \rho_i}{\rho},$$

the eq (17) can be rearranged as:

$$(n-1) = \sum(n_i - 1)\phi_i \qquad ...(18)$$

Lorentz-Lorenz relation (L-L): Lorentz and Lorenz[18,19] proposed mixing rule for evaluating the refractive index of liquid mixture, which can be represented as:

$$\left[\frac{(n^2-1)}{(n^2+2)}\frac{1}{\rho}\right] = \left[\sum\left(\frac{(n_i^2-1)}{(n_i^2+2)}\frac{W_i}{\rho_i}\right)\right] \qquad ...(19)$$

The above equation can be rearranged as:

$$\left(\frac{(n^2-1)}{(n^2+2)}\right) = \sum\left(\frac{(n_i^2-1)}{(n_i^2+2)}\phi_i\right) \qquad ...(20)$$

Eykman relation (Eyk): Eykman relation[15] for the evaluation of refractive index of liquid mixture can be expressed as:

$$\frac{(n^2-1)}{(n+0.4)} = \sum\left(\frac{(n_i^2-1)}{(n_i+0.4)}\phi_i\right) \qquad ...(21)$$

be used to evaluate theoretical values of molar refractivity and then theoretical deviations in refractive index using eq (15). Some important mixing rules are discussed here.

Dale-Gladstone relation (D-G): Based upon strict volume additivity assumption, Dale et al[16] proposed the mixing rule, which is given by

$$\left[\frac{n-1}{\rho}\right] = \sum\left(\frac{n_i - 1}{\rho_i} W_i\right) \qquad ...(17)$$

where n and ρ are refractive index and density of liquid mixture, and n_i and W_i are the refractive index and weight fraction of i^{th} component of the mixture. Since, weight fraction and volume fraction (ϕ_i) are related with the relation

$$W_i = \frac{\phi_i \rho_i}{\rho},$$

the eq (17) can be rearranged as:

$$(n-1) = \sum (n_i - 1)\phi_i \qquad ...(18)$$

Lorentz-Lorenz relation (L-L): Lorentz and Lorenz[18,19] proposed mixing rule for evaluating the refractive index of liquid mixture, which can be represented as:

$$\left[\frac{(n^2-1)}{(n^2+2)}\frac{1}{\rho}\right] = \left[\sum\left(\frac{(n_i^{\,2}-1)}{(n_i^{\,2}+2)}\frac{W_i}{\rho_i}\right)\right] \qquad ...(19)$$

The above equation can be rearranged as:

$$\left(\frac{(n^2-1)}{(n^2+2)}\right) = \sum\left(\frac{(n_i^{\,2}-1)}{(n_i^{\,2}+2)}\phi_i\right) \qquad ...(20)$$

Eykman relation (Eyk): Eykman relation[15] for the evaluation of refractive index of liquid mixture can be expressed as:

$$\frac{(n^2-1)}{(n+0.4)} = \sum\left(\frac{(n_i^{\,2}-1)}{(n_i+0.4)}\phi_i\right) \qquad ...(21)$$

be used to evaluate theoretical values of molar refractivity and then theoretical deviations in refractive index using eq (15). Some important mixing rules are discussed here.

Dale-Gladstone relation (D-G): Based upon strict volume additivity assumption, Dale et al[16] proposed the mixing rule, which is given by

$$\left[\frac{n-1}{\rho}\right] = \sum\left(\frac{n_i - 1}{\rho_i} W_i\right) \qquad ...(17)$$

where n and ρ are refractive index and density of liquid mixture, and n_i and W_i are the refractive index and weight fraction of i^{th} component of the mixture. Since, weight fraction and volume fraction (ϕ_i) are related with the relation

$$W_i = \frac{\phi_i \rho_i}{\rho},$$

the eq (17) can be rearranged as:

$$(n-1) = \sum (n_i - 1)\phi_i \qquad ...(18)$$

Lorentz-Lorenz relation (L-L): Lorentz and Lorenz[18,19] proposed mixing rule for evaluating the refractive index of liquid mixture, which can be represented as:

$$\left[\frac{(n^2-1)}{(n^2+2)}\frac{1}{\rho}\right] = \left[\sum\left(\frac{(n_i^2-1)}{(n_i^2+2)}\frac{W_i}{\rho_i}\right)\right] \qquad ...(19)$$

The above equation can be rearranged as:

$$\left(\frac{(n^2-1)}{(n^2+2)}\right) = \sum\left(\frac{(n_i^2-1)}{(n_i^2+2)}\phi_i\right) \qquad ...(20)$$

Eykman relation (Eyk): Eykman relation[15] for the evaluation of refractive index of liquid mixture can be expressed as:

$$\frac{(n^2-1)}{(n+0.4)} = \sum\left(\frac{(n_i^2-1)}{(n_i+0.4)}\phi_i\right) \qquad ...(21)$$

Newton relation (NR): Newton relation[13] for the evaluation of refractive index of liquid mixtures can be expressed as:

$$(n^2 - 1) = \sum (n_i^2 - 1)\phi_i \qquad ...(22)$$

Heller relation (HR): For the evaluation of refractive index of binary liquid mixtures, Heller relation[14] can be expressed as:

$$\left(\frac{(n - n_1)}{n_1}\right) = \frac{3}{2}\left(\frac{(n_2/n_1)^2 - 1}{(n_2/n_1)^2 + 2}\right)\phi_2 \qquad ...(23)$$

Weiner relation (WR): For the evaluation of refractive index of binary liquid mixtures, Weiner relation[17] can be expressed as:

$$\frac{(n^2 - n_1^2)}{(n^2 + 2n_1^2)} = \frac{(n_2^2 - n_1^2)}{(n_2^2 + 2n_1^2)}\phi_2 \qquad ...(24)$$

4.4 Results and Discussion

The properties of pure liquids used as the components of binary and ternary liquid mixtures are listed in table-1. The experimental values of ultrasonic velocity (u) and computed values of the same, using some empirical and statistical relations, have been depicted in table-2. The results thus obtained have been graphically represented in fig 1. The eqs (4), (5), (6), (11) and (12) were utilised to evaluate the ultrasonic velocity of the liquid mixtures. Table-2 also lists the percentage differences in the values of ultrasonic velocity obtained from these relations, as compared with the experimental values for the same. Ideal values of ultrasonic velocity of liquids mixtures are also shown in table-2 for comparison, which were calculated using the relation, $u_{calc}(IDL)=\Sigma x_i u_i$. These results show that, Nomoto relation (NR), Junjie relation (JR), Collision Factor Theory (CFT) and the relation based upon Flory Theory (Flory) provide satisfactory results and can be considered to be good methods for evaluation of ultrasonic velocity of the liquid mixtures of concern. Van Dael - Vangeel relation (VD) gives larger deviations in the systems under investigation.

However, wherever the thermal expansion coefficient (α) and isothermal compressibility (β_T) data of pure components are available, we recommend the use of Flory statistical method for the evaluation of ultrasonic velocity in the liquid mixtures. This is because this method clearly includes the interaction parameter (X_{ij}), which is a very important aspect of this method.

The experimental values of refractive index (n) and computed values of the same, using some mixing rules, have been depicted in table-3. The eqs (18), (20), (21), (22), (23) and (24) were utilised to evaluate the refractive index of the liquid mixtures. Table-3 also lists the percentage differences in the values of refractive index obtained from these relations, as compared with the experimental values for the same. These results show that all these methods are nearly approximate in nature. This might be because of the reason that all these relations directly or indirectly are related with volume fraction additivity assumptions in liquid mixtures.

Molar sound velocity (R), which is also known as Rao's constant, and its deviation from volume fraction average (ΔR) have also been computed using eqs (2) and (13). The computed values of the same are listed in table-4. Table–4 also lists the experimental values of molar refractivity (R_m), its deviation from volume fraction average $(\Delta R_m)_{expt}$ and computed values of theoretical deviations of molar refractivity from volume fraction average $\{(\Delta R_m)_{theo}\}$. Though theoretical values of refractive index are in close agreement with the experimental values, slight higher deviations are observed in the ΔR_{theo} values. These results have been graphically presented in fig 2. The low positive values of ΔR and ΔR_m in ethanol + N,N-DMF as compared to ethanol + cyclohexane may be regarded as an indication of molecular interaction between N,N-DMF and ethanol, possibly due to hydrogen bonding. The high positive values of ΔR and ΔR_m in ethanol + cyclohexane may be regarded as a weak interaction between the component molecules, possibly the structure breaking type interaction. In ternary liquid mixture ethanol+ N,N-DMF+ cyclohexane, values of ΔR and ΔR_m increase first up to the point when $x_{cyclohexane} \approx 0.4$ and then decrease.

Interesting similarity between ΔR and ΔR_m can be observed. Though ΔR_m values are comparatively small, the variation pattern of ΔR and ΔR_m with change in the mole fraction of one of the component is nearly same in all the systems under investigation.

4.5 References

1. Eyring H & Hirschfelder J O, *J Phys Chem*, **41** (1937) 249.
2. Schaaffs W, *Z Physik*, **114** (1939) 110.
3. Rao M R, *J Chem Phys*, **9** (1941) 682.
4. Auerbach E N, *Experientia*, **4** (1948) 473.
5. Wada Y, *J Phys Soc Jpn*, **4** (1949) 280.
6. Jacobson B, *J Chem Phys*, **19** (1950) 927; **20** (1952) 927.
7. Jacobson B, *Acta Chem Scand*, **5** (1951) 1214.
8. Nomoto O, *J Phys Soc Jpn*, **13** (1958) 1528.
9. Nutsch R & Kuhnkies S, *Acustica*, **15** (1965) 383.
10. Rao R V G & Vankateshaiah V, *Z Phys Chem*, **242** (1969)193.
11. Van Dael W & Vangeel E, *Proc 1st int conf on calometry and thermodynamics*, Warsaw (1969).
12. Junjie Z, *J Chem Uni Sci Tech*, **14** (1984) 298.
13. Kurtz S S & Ward A L, *J Franklin Inst*, **222** (1936) 563.
14. Heller W, *Phys Rev*, **68** (1945) 5.
15. Bottcher C J F, *Theory of Electric Polarization*, Elsevier, Amsterdam (1952).
16. Dale D & Gladstone F, *Philos Trans R Soc Lond*, **148** (1958) 887.
17. Weiner O, *Leipz Ber*, **62** (1910) 256.
18. Lorentz H A, *Weid Ann*, **9** (1880) 641.
19. Lorenz L, *Weid Ann*, **11** (1880) 70.
20. Reese B O, Seely L B, Shaw R & Tegg D, *J Chem Eng Data*, **15(1)** (1970) 140.
21. Mishra R L & Pandey J D, *Ind J Pure & Appl Phys*, **15(7)** (1977) 505.
22. Aminabhavi T M & Munk P, *Macromolecules*, **12** (1979) 1186.
23. Pandey J D & Mishra K, *Acoustics Letters*, **6(10)** (1983) 148.

24. Pandey J D, Shrivastava V N, Vyas V & Panta N, *Ind J Pure & Appl Phys*, **25** (1987) 467.
25. Islam M R & Quadri S K, *Acoustics Letters*, **11(12)** (1988) 237.
26. Oswal S L & Palsanawala P P, *Acoustics Letters*, **13(4)** (1989) 66.
27. Narayana K L & Swamy K M, *J Chem Eng Data*, **34** (1989) 19.
28. Oswal S L, *Acoustics Letters*, **14(1)** (1990) 17.
29. Khanwalkar M S, Murty J S & Despande D D, *Acoustics Letters*, **13(7)** (1990) 121.
30. Nakai H, Tamura K, Ogawa H, Murakami S & Toshiyaso Y, *Thermochem Acta*, **177** (1991) 317.
31. Dhanalakshmi A, Lalitha V & Hema R, *J Acoust Soc Ind*, **XX(1-4)** (1992) 125.
32. Aralaguppi M I, Aminabhavi T M, Harogoppad S B & Balundgi R H, *J Chem Eng Data*, **37** (1992) 298.
33. Pandey J D, Shukla A K, Gupta S & Pandey S, *Fluid Phase Equilibria*, **103** (1995) 285.
34. Aminabhavi T M, Phayde H T S, Khinnavar S & Gopalakrishna B, *J Chem Eng Data*, **39** (1994) 251.
35. Pal A & Singh Y P, *J Chemical Thermodyn*, **28** (1996) 143.
36. Hu J, Tamura K & Murakami S, *Fluid Phase Equilibria*, **134** (1997) 239.
37. Sastry N V, Patel M C & Patel S R, *Fluid Phase Equilibria*, **155** (1999) 261.
38. Pal A, Sharma S & Kumar A, *Ind J Pure & Appl Phys*, 38 (2000) 174.
39. Lee J W, Kim J S, Lee Y W, Baek Y S & Pang H S, *J Chem Thermodyn*, **33(1)** (2001) 1527.
40. Rodriguez A, Canosa J & Tojo J, *J Chem Thermodyn*, **33(10)** (2001) 1383.
41. Gomez-Diaz D, Mejuto J C & Navaza J M, *J Chem Eng Data*, **46** (2001) 720.
42. Diaz C, Orge B, Marino G & Tojo J, *J Chem Thermodyn*, **33(9)** (2001) 1015.
43. Nayak J N, Aralaguppi M I & Aminabhavi T M, *J Chem Eng Data*, **47(4)** (2002) 964.
44. Rosa J M, Gonzalez C, Landaluce S O & Lanz J, *J Chem Eng Data*, **47(5)** (2002) 1123.

45. Dutor S, Lagourette B & Daridon J L, J Chem Thermodyn, **34(4)** (2002) 475.

46. Pal A & Bhardwaj R K, *J Chem Thermodyn*, **34(8)** (2002) 1157.

47. Comeli F, Francesconi S & Castellari C, *J Chem Eng Data*, **47(5)** (2002) 1226.

48. Gomez-Diaz D, Mejuto J C, Navaza J M & Alvarez A R, *J Chem Eng Data*, **47(4)** (2002) 872.

Table-1

Properties of pure compounds at 308.15 K

Compounds	ρ_{expt} kg m^{-3}	u_{expt} m s^{-1}	n_{expt}	V 10^{-6} m^3 mol^{-1}	α 10^{-3} K^{-1}	β_T 10^{-11} m^2 N^{-1}	β_S 10^{-11} m^2 N^{-1}	C_P J mol^{-1} K^{-1}
Ethanol	777.9	1117.46	1.357	59.22	1.125	123.21	102.95	114.0
N,N-DMF	935.5	1432.00	1.423	78.13	0.879	64.34	52.13	152.4
Cyclohexane	764.2	1209.14	1.420	110.13	1.246	122.45	89.50	159.9

Table-2

Experimental and calculated values of ultrasonic velocity (u) in binary and ternary liquid mixtures, at 308.15 K

2. a) Binary Liquid Mixture: Ethanol (1) + N,N-dimethylformamide (N,N-DMF) (2)

x_1	x_2	u_{expt}	u_{calc} (m s^{-1})						% Diff. in u					
		m s^{-1}	*Flory*	*VD*	*NOM*	*JR*	*CFT*	*IDL*	*Flory*	*VD*	*NOM*	*JR*	*CFT*	*IDL*
0.0000	1.0000	1432.00	1431.97	1432.00	1432.00	1431.99	1432.00	1432.00	0.00	0.00	0.00	0.00	0.00	0.00
0.0506	0.9494	1417.14	1418.55	1390.22	1418.81	1410.26	1421.50	1416.08	-0.10	1.90	-0.12	0.49	-0.31	0.07
0.1261	0.8739	1401.57	1398.25	1337.45	1398.66	1379.28	1405.36	1392.34	0.24	4.57	0.21	1.59	-0.27	0.66
0.2018	0.7982	1386.00	1377.16	1293.73	1377.88	1349.84	1388.40	1368.53	0.64	6.66	0.59	2.61	-0.17	1.26
0.3613	0.6387	1349.14	1331.07	1223.90	1332.12	1292.67	1345.49	1318.36	1.34	9.28	1.26	4.19	0.27	2.28
0.5009	0.4991	1306.29	1288.50	1181.08	1289.72	1247.47	1304.62	1274.45	1.36	9.59	1.27	4.50	0.13	2.44
0.6623	0.3377	1256.00	1236.47	1147.23	1237.73	1200.29	1251.89	1223.68	1.55	8.66	1.45	4.44	0.33	2.57
0.8281	0.1719	1199.43	1179.84	1126.38	1180.73	1157.04	1191.39	1171.53	1.63	6.09	1.56	3.53	0.67	2.33
0.9032	0.0969	1167.29	1153.06	1120.98	1153.65	1139.12	1161.80	1147.92	1.22	3.97	1.17	2.41	0.47	1.66
0.9782	0.0218	1135.14	1125.53	1117.92	1125.73	1122.21	1129.71	1124.32	0.85	1.52	0.83	1.14	0.48	0.95
1.0000	0.0000	1117.46	1117.44	1117.46	1117.46	1117.49	1117.46	1117.46	0.00	0.00	0.00	0.00	0.00	0.00

2. b) Binary liquid mixture: Ethanol (1) + Cyclohexane (2)

x_1	x_2	u_{expt}	u_{calc} ($m\ s^{-1}$)						% Diff. in u					
		$m\ s^{-1}$	*Flory*	*VD*	*NOM*	*JR*	*CFT*	*IDL*	*Flory*	*VD*	*NOM*	*JR*	*CFT*	*IDL*
0.0000	1.0000	1209.14	1209.16	1209.14	1209.14	1209.13	1209.14	1209.14	0.00	0.00	0.00	0.00	0.00	0.00
0.0542	0.9458	1200.29	1203.45	1188.13	1206.33	1206.10	1205.73	1204.17	-0.26	1.01	-0.50	-0.48	-0.45	-0.32
0.1278	0.8722	1188.57	1195.64	1163.88	1202.28	1201.77	1200.86	1197.42	-0.59	2.08	-1.15	-1.11	-1.03	-0.74
0.2027	0.7973	1179.14	1187.64	1143.59	1197.86	1197.07	1195.72	1190.56	-0.72	3.01	-1.59	-1.52	-1.41	-0.97
0.3648	0.6352	1160.29	1170.29	1112.28	1187.07	1185.76	1183.60	1175.70	-0.86	4.14	-2.31	-2.20	-2.01	-1.33
0.5004	0.4996	1148.57	1156.01	1097.26	1176.50	1174.88	1172.82	1163.26	-0.65	4.47	-2.43	-2.29	-2.11	-1.28
0.6640	0.3360	1134.29	1139.75	1090.95	1161.31	1159.58	1157.60	1148.26	-0.48	3.82	-2.38	-2.23	-2.05	-1.23
0.8315	0.1685	1121.43	1125.67	1097.29	1142.08	1140.76	1140.34	1132.91	-0.38	2.15	-1.84	-1.72	-1.69	-1.02
0.9034	0.0966	1120.29	1121.13	1104.11	1132.33	1131.44	1131.92	1126.32	-0.07	1.44	-1.07	-1.00	-1.04	-0.54
0.9763	0.0237	1118.29	1118.05	1113.72	1121.32	1121.08	1122.10	1119.63	0.02	0.41	-0.27	-0.25	-0.34	-0.12
1.0000	0.0000	1117.46	1117.44	1117.46	1117.46	1117.49	1117.46	1117.46	0.00	0.00	0.00	0.00	0.00	0.00

2. c) Binary Liquid Mixture: N,N-DMF (1) + Cyclohexane (2)
[Only in Miscibility Range]

x_1	x_2	u_{expt}	u_{calc} ($m\ s^{-1}$)						% Diff. in u					
		$m\ s^{-1}$	*Flory*	*VD*	*NOM*	*JR*	*CFT*	*IDL*	*Flory*	*VD*	*NOM*	*JR*	*CFT*	*IDL*
0.0000	1.0000	1209.14	1209.16	1209.14	1209.14	1209.13	1209.14	1209.14	0.00	0.00	0.00	0.00	0.00	0.00
0.0293	0.9707	1209.43	1214.19	1214.67	1213.56	1211.61	1211.51	1215.67	-0.39	-0.43	-0.34	-0.18	-0.17	-0.52
0.0402	0.9598	1210.29	1216.11	1216.74	1215.22	1212.57	1212.71	1218.10	-0.48	-0.53	-0.41	-0.19	-0.20	-0.65
0.0548	0.9452	1210.57	1218.71	1219.52	1217.47	1213.87	1214.54	1221.35	-0.67	-0.74	-0.57	-0.27	-0.33	-0.89
0.8443	0.1557	1381.43	1389.05	1391.97	1383.95	1362.53	1389.07	1397.30	-0.55	-0.76	-0.18	1.37	-0.55	-1.15
0.9001	0.0999	1391.43	1403.99	1406.05	1400.37	1384.48	1403.69	1409.74	-0.90	-1.05	-0.64	0.50	-0.88	-1.32
0.9592	0.0408	1406.00	1420.37	1421.29	1418.72	1411.14	1419.67	1422.91	-1.02	-1.09	-0.90	-0.37	-0.97	-1.20
1.0000	0.0000	1432.00	1431.97	1432.00	1432.00	1431.99	1432.00	1432.00	0.00	0.00	0.00	0.00	0.00	0.00

2. d) Ternary Liquid Mixture: Ethanol (1) + N,N-DMF (2) + Cyclohexane (3)

x_1	x_2	x_3	u_{expt}	u_{calc} (m s^{-1})						% Diff. in u					
			m s^{-1}	*Flory*	*VD*	*NOM*	*JR*	*CFT*	*IDL*	*Flory*	*VD*	*NOM*	*JR*	*CFT*	*I*
0.4675	0.4682	0.0643	1285.43	1279.28	1178.39	1281.92	1242.48	1293.21	1270.62	0.48	8.33	0.27	3.34	-0.61	1.
0.4305	0.4314	0.1381	1264.29	1269.54	1175.79	1273.31	1237.20	1280.73	1265.81	-0.42	7.00	-0.71	2.14	-1.30	-0.
0.3940	0.3949	0.2111	1249.43	1260.85	1174.04	1265.48	1232.72	1267.77	1261.03	-0.91	6.03	-1.28	1.34	-1.47	-0.
0.3071	0.3076	0.3853	1222.29	1243.63	1173.13	1249.09	1224.31	1248.91	1249.54	-1.75	4.02	-2.19	-0.17	-2.18	-2.
0.2416	0.2420	0.5164	1203.43	1233.40	1175.58	1238.59	1219.60	1234.31	1240.92	-2.49	2.31	-2.92	-1.34	-2.57	-3.
0.2056	0.2059	0.5885	1197.71	1228.56	1178.07	1233.36	1217.44	1226.10	1236.18	-2.58	1.64	-2.98	-1.65	-2.37	-3.
0.1451	0.1455	0.7094	1195.14	1221.57	1184.19	1225.36	1214.40	1217.47	1228.26	-2.21	0.92	-2.53	-1.61	-1.87	-2.
0.1232	0.1234	0.7534	1194.86	1219.31	1186.98	1222.63	1213.43	1215.33	1225.35	-2.05	0.66	-2.32	-1.55	-1.71	-2.
0.0703	0.0704	0.8593	1195.43	1214.50	1195.12	1216.50	1211.37	1209.90	1218.38	-1.60	0.03	-1.76	-1.33	-1.21	-1.

Table - 3

Experimental and calculated values of refractive index (n) in binary and ternary liquid mixtures, at 308.15 K

3. a) Binary Liquid Mixture: Ethanol (1) + N,N-dimethylformamide (N,N-DMF) (2)

x_1	x_2	n	$n_{(calc)}$						% Diff. in n					
		Expt	*D-G*	*L-L*	*Eyk*	*WR*	*HR*	*NW*	*D-G*	*L-L*	*Eyk*	*WR*	*HR*	*NW*
0.0000	1.0000	1.423	1.4230	1.4230	1.4230	1.4230	1.4224	1.4230	0.00	0.00	0.00	0.00	0.04	0.00
0.0506	0.9494	1.421	1.4204	1.4204	1.4204	1.4204	1.4199	1.4205	0.04	0.04	0.04	0.04	0.08	0.04
0.1261	0.8739	1.418	1.4165	1.4164	1.4164	1.4164	1.4160	1.4166	0.11	0.11	0.11	0.11	0.14	0.10
0.2018	0.7982	1.416	1.4124	1.4122	1.4123	1.4123	1.4119	1.4126	0.25	0.27	0.26	0.26	0.29	0.24
0.3613	0.6387	1.409	1.4032	1.4029	1.4031	1.4031	1.4028	1.4035	0.41	0.43	0.42	0.42	0.44	0.39
0.5009	0.4991	1.401	1.3945	1.3941	1.3944	1.3943	1.3942	1.3949	0.46	0.49	0.47	0.48	0.49	0.44
0.6623	0.3377	1.388	1.3835	1.3832	1.3834	1.3834	1.3833	1.3839	0.32	0.35	0.33	0.33	0.34	0.30
0.8281	0.1719	1.375	1.3712	1.3709	1.3711	1.3711	1.3711	1.3715	0.28	0.30	0.28	0.28	0.28	0.25
0.9032	0.0969	1.368	1.3652	1.3650	1.3651	1.3651	1.3651	1.3654	0.20	0.22	0.21	0.21	0.21	0.19
0.9782	0.0218	1.361	1.3589	1.3588	1.3589	1.3589	1.3589	1.3589	0.15	0.16	0.15	0.15	0.15	0.15
1.0000	0.0000	1.357	1.3570	1.3570	1.3570	1.3570	1.3570	1.3570	0.00	0.00	0.00	0.00	0.00	0.00

3. b) Binary Liquid Mixture: Ethanol (1) + Cyclohexane (2)

x_1	x_2	n	$n_{(calc)}$						% Diff. In n					
		Expt	*D-G*	*L-L*	*Eyk*	*WR*	*HR*	*NW*	*D-G*	*L-L*	*Eyk*	*WR*	*HR*	*NW*
0.0000	1.0000	1.420	1.4200	1.4200	1.4200	1.4200	1.4195	1.4200	0.00	0.00	0.00	0.00	0.04	0.00
0.0542	0.9458	1.419	1.4181	1.4181	1.4181	1.4181	1.4176	1.4182	0.06	0.06	0.06	0.06	0.10	0.06
0.1278	0.8722	1.418	1.4154	1.4153	1.4154	1.4154	1.4149	1.4155	0.18	0.19	0.18	0.18	0.22	0.18
0.2027	0.7973	1.416	1.4124	1.4123	1.4124	1.4124	1.4120	1.4126	0.25	0.26	0.25	0.25	0.28	0.24
0.3648	0.6352	1.403	1.4051	1.4049	1.4051	1.4050	1.4047	1.4054	-0.15	-0.14	-0.15	-0.14	-0.12	-0.17
0.5004	0.4996	1.392	1.3979	1.3976	1.3978	1.3978	1.3976	1.3983	-0.42	-0.40	-0.42	-0.42	-0.40	-0.45
0.6640	0.3360	1.379	1.3875	1.3872	1.3874	1.3874	1.3873	1.3879	-0.62	-0.59	-0.61	-0.61	-0.60	-0.65
0.8315	0.1685	1.368	1.3742	1.3740	1.3742	1.3741	1.3741	1.3745	-0.45	-0.44	-0.45	-0.45	-0.45	-0.48
0.9034	0.0966	1.363	1.3674	1.3673	1.3674	1.3674	1.3674	1.3677	-0.32	-0.32	-0.32	-0.32	-0.32	-0.34
0.9763	0.0237	1.360	1.3597	1.3597	1.3597	1.3597	1.3597	1.3598	0.02	0.02	0.02	0.02	0.02	0.01
1.0000	0.0000	1.357	1.3570	1.3570	1.3570	1.3570	1.3570	1.3570	0.00	0.00	0.00	0.00	0.00	0.00

3. c) Binary Liquid Mixture: N,N-DMF (1) + Cyclohexane (2) [Only in Miscibility Range]

x_1	x_2	n	$n_{(calc)}$						% Diff. in n					
		Expt	*D-G*	*L-L*	*Eyk*	*WR*	*HR*	*NW*	*D-G*	*L-L*	*Eyk*	*WR*	*HR*	*NW*
0.0000	1.0000	1.420	1.4200	1.4200	1.4200	1.4200	1.4200	1.4200	0.00	0.00	0.00	0.00	0.00	0.00
0.0293	0.9707	1.420	1.4201	1.4201	1.4201	1.4201	1.4201	1.4201	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01
0.0402	0.9598	1.421	1.4201	1.4201	1.4201	1.4201	1.4201	1.4201	0.06	0.06	0.06	0.06	0.06	0.06
0.0548	0.9452	1.421	1.4201	1.4201	1.4201	1.4201	1.4201	1.4201	0.06	0.06	0.06	0.06	0.06	0.06
0.8443	0.1557	1.422	1.4224	1.4224	1.4224	1.4224	1.4224	1.4224	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03
0.9001	0.0999	1.422	1.4226	1.4226	1.4226	1.4226	1.4226	1.4226	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04
0.9592	0.0408	1.422	1.4228	1.4228	1.4228	1.4228	1.4228	1.4228	-0.06	-0.06	-0.06	-0.06	-0.06	-0.06
1.0000	0.0000	1.423	1.4230	1.4230	1.4230	1.4230	1.4230	1.4230	0.00	0.00	0.00	0.00	0.00	0.00

3. d) Ternary Liquid Mixture: Ethanol (1) + N,N-DMF (2) + Cyclohexane (3)

x_1	x_2	x_3	n	$n_{(calc)}$				% Diff. in n			
			Expt	*D-G*	*L-L*	*Eyk*	*NW*	*D-G*	*L-L*	*Eyk*	*NW*
0.4675	0.4682	0.0643	1.402	1.3971	1.3967	1.3970	1.3975	0.35	0.38	0.36	0.32
0.4305	0.4314	0.1381	1.403	1.3998	1.3994	1.3997	1.4001	0.19	0.22	0.20	0.17
0.3940	0.3949	0.2111	1.403	1.4022	1.4019	1.4021	1.4025	0.06	0.08	0.06	0.04
0.3071	0.3076	0.3853	1.405	1.4073	1.4071	1.4072	1.4076	-0.16	-0.15	-0.16	-0.19
0.2416	0.2420	0.5164	1.407	1.4106	1.4104	1.4106	1.4108	-0.26	-0.24	-0.26	-0.27
0.2056	0.2059	0.5885	1.412	1.4123	1.4121	1.4122	1.4124	-0.02	-0.01	-0.01	-0.03
0.1451	0.1455	0.7094	1.416	1.4148	1.4147	1.4148	1.4149	0.08	0.09	0.08	0.08
0.1232	0.1234	0.7534	1.418	1.4157	1.4156	1.4157	1.4158	0.16	0.17	0.16	0.16
0.0703	0.0704	0.8593	1.420	1.4176	1.4176	1.4176	1.4177	0.17	0.17	0.17	0.16

Table - 4

Molar sound velocity (R), molar refraction (R_m) and their deviations in binary and ternary liquid mixtures at 308.15K

4. a) Binary Liquid Mixture: Ethanol (1) + N,N-dimethylformamide (N,N-DMF) (2)

x_1	x_2	$R/10^{-6}$	R_m	ΔR	ΔR_m	$(\Delta Rm)_{theo}$ / 10^{-6} m^3mol^{-1}					
		$m^{10/3} s^{-1/3} mol^{-1}$	$10^{-6} m^3 mol^{-1}$	$m^{10/3} s^{-1/3} mol^{-1}$	$10^{-6} m^3 mol^{-1}$	*D-G*	*L-L*	*Eyk*	*WR*	*HR*	*NW*
0.0000	1.0000	880.64	19.90	0.00	0.00	0.00	0.00	0.00	0.00	-0.02	0.00
0.0506	0.9494	865.79	19.55	4.52	0.08	0.10	0.10	0.10	0.10	0.08	0.10
0.1261	0.8739	845.04	19.03	9.37	0.18	0.24	0.24	0.24	0.24	0.22	0.24
0.2018	0.7982	824.39	18.56	13.46	0.23	0.37	0.37	0.37	0.37	0.35	0.37
0.3613	0.6387	783.21	17.52	17.58	0.29	0.51	0.51	0.51	0.51	0.50	0.51
0.5009	0.4991	745.64	16.57	20.03	0.33	0.57	0.57	0.57	0.57	0.56	0.57
0.6623	0.3377	703.36	15.38	18.19	0.37	0.53	0.53	0.53	0.53	0.52	0.53
0.8281	0.1719	660.23	14.22	11.51	0.24	0.36	0.36	0.36	0.36	0.36	0.36
0.9032	0.0969	639.86	13.68	7.66	0.15	0.24	0.24	0.24	0.24	0.24	0.24
0.9782	0.0218	620.26	13.16	1.87	0.01	0.08	0.08	0.08	0.08	0.08	0.08
1.0000	0.0000	614.53	12.97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

4. b) Binary liquid mixture: Ethanol (1) + Cyclohexane (2)

x_1	x_2	$R/10^{-6}$	R_m	ΔR	ΔR_m	$(\Delta Rm)_{theo}$ / 10^{-6} m^3 mol^{-1}					
		$m^{10/3}$ $s^{-1/3}$ mol^{-1}	10^{-6} m^3 mol^{-1}	$m^{10/3}$ $s^{-1/3}$ mol^{-1}	10^{-6} m^3 mol^{-1}	*D-G*	*L-L*	*Eyk*	*WR*	*HR*	*NW*
0.0000	1.0000	1173.27	27.87	0.00	0.00	0.00	0.00	0.00	0.00	-0.03	0.00
0.0542	0.9458	1141.71	27.13	14.86	0.29	0.35	0.35	0.35	0.35	0.32	0.35
0.1278	0.8722	1099.10	26.15	33.36	0.63	0.78	0.78	0.78	0.78	0.75	0.78
0.2027	0.7973	1056.57	25.10	49.50	0.98	1.17	1.17	1.17	1.17	1.15	1.17
0.3648	0.6352	965.27	22.42	76.16	1.94	1.83	1.83	1.83	1.83	1.81	1.83
0.5004	0.4996	889.75	20.23	87.93	2.42	2.15	2.15	2.15	2.15	2.14	2.15
0.6640	0.3360	798.96	17.70	86.45	2.49	2.14	2.14	2.14	2.14	2.12	2.14
0.8315	0.1685	705.75	15.29	61.71	1.76	1.53	1.53	1.53	1.53	1.52	1.53
0.9034	0.0966	666.57	14.27	40.65	1.17	1.02	1.02	1.02	1.02	1.01	1.02
0.9763	0.0237	626.83	13.33	11.84	0.29	0.30	0.30	0.30	0.30	0.30	0.30
1.0000	0.0000	614.53	12.97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

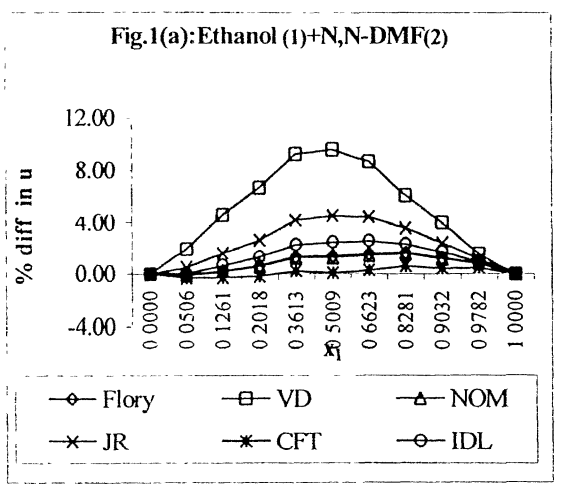
4. c) Binary Liquid Mixture: N,N-DMF (1) + Cyclohexane (2)
[Only in Miscibility Range]

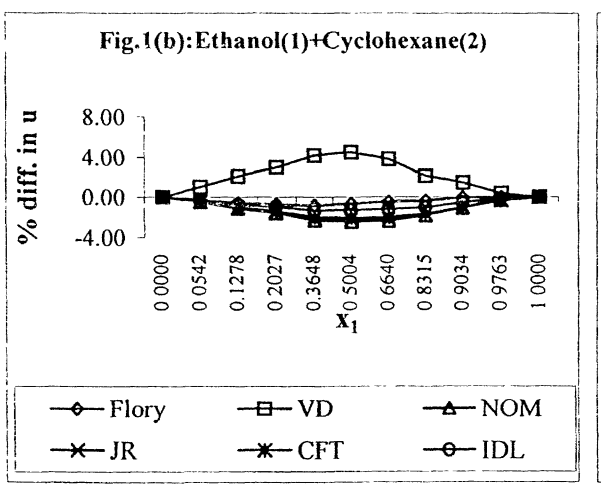
x_1	x_2	$R/10^{-6}$	R_m	ΔR	ΔR_m	$(\Delta Rm)_{theo}$ / 10^{-6} $m^3 mol^{-1}$					
		$m^{10/3}$ $s^{-1/3}$ mol^{-1}	10^{-6} m^3 mol^{-1}	$m^{10/3}$ $s^{-1/3}$ mol^{-1}	10^{-6} m^3 mol^{-1}	*D-G*	*L-L*	*Eyk*	*WR*	*HR*	*NW*
0.0000	1.0000	1173.27	27.87	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.0293	0.9707	1165.59	27.69	1.55	-0.40	0.01	0.01	0.01	0.01	0.01	0.01
0.0402	0.9598	1162.66	27.67	2.16	-0.60	0.02	0.02	0.02	0.02	0.02	0.02
0.0548	0.9452	1158.28	27.56	3.43	-0.79	0.05	0.05	0.05	0.05	0.05	0.05
0.8443	0.1557	923.61	21.07	17.41	-15.32	0.45	0.45	0.45	0.45	0.45	0.45
0.9001	0.0999	906.74	20.64	13.49	-16.87	0.31	0.31	0.31	0.31	0.31	0.31
0.9592	0.0408	889.73	20.18	7.46	-18.61	0.13	0.13	0.13	0.13	0.13	0.13
1.0000	0.0000	880.64	19.90	0.00	-19.90	0.00	0.00	0.00	0.00	0.00	0.00

4. d) Ternary Liquid Mixture: Ethanol (1) + N,N-DMF (2) + Cyclohexane (3)

x_1	x_2	x_3	$R/10^{-6}$	R_m	ΔR	ΔR_m	$(\Delta Rm)_{theo} / 10^{-6}\ m^3\ mol^{-1}$			
			$m^{10/3}\ s^{-1/3}\ mol^{-1}$	$10^{-6}\ m^3\ mol^{-1}$	$m^{10/3}\ s^{-1/3}\ mol^{-1}$	$10^{-6}\ m^3\ mol^{-1}$	*D-G*	*L-L*	*Eyk*	*NW*
0.4675	0.4682	0.0643	772.53	17.30	33.90	0.70	0.89	0.89	0.89	0.88
0.4305	0.4314	0.1381	803.30	18.11	45.99	1.04	1.15	1.15	1.15	1.15
0.3940	0.3949	0.2111	835.69	18.93	52.63	1.27	1.30	1.30	1.30	1.29
0.3071	0.3076	0.3853	907.86	20.81	62.30	1.59	1.49	1.49	1.49	1.48
0.2416	0.2420	0.5164	963.69	22.30	59.43	1.53	1.35	1.35	1.35	1.34
0.2056	0.2059	0.5885	996.14	23.34	53.46	1.20	1.19	1.19	1.19	1.17
0.1451	0.1455	0.7094	1049.02	24.81	41.39	0.83	0.90	0.90	0.90	0.87
0.1232	0.1234	0.7534	1067.72	25.36	36.53	0.66	0.78	0.78	0.78	0.75
0.0703	0.0704	0.8593	1113.63	26.55	21.90	0.30	0.43	0.43	0.43	0.41

Fig. 1: Percentage difference in ultrasonic velocity (u) in liquid mixtures at 308.15K (as calculated using various mixing rules)





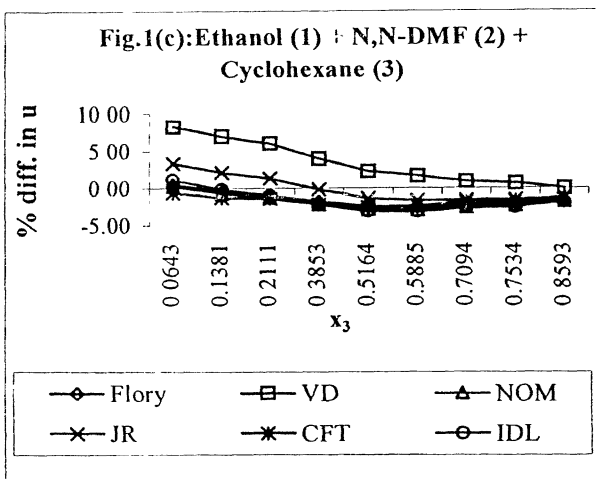


Fig. 2: Deviations in molar sound velocity (ΔR) and molar refractivity (ΔRm) from volume fraction average in binary and ternary liquid mixtures at 308.15 K

Fig. 2. (a): Deviations in molar sound velocity (ΔR) in binary and ternary liquid mixtures

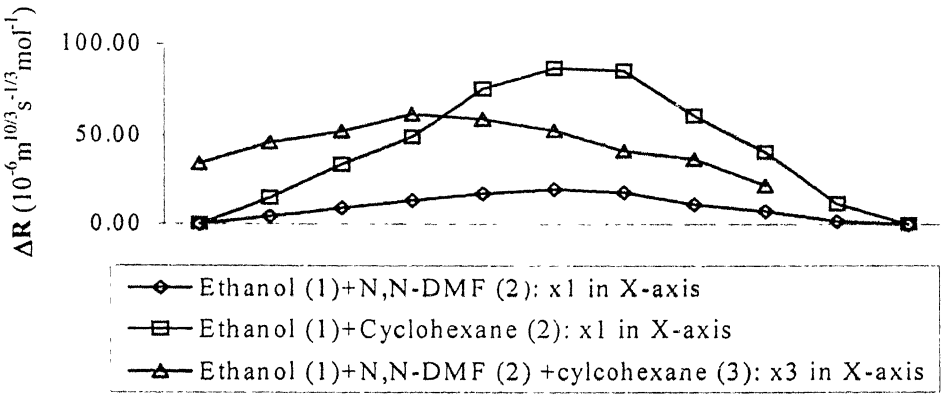
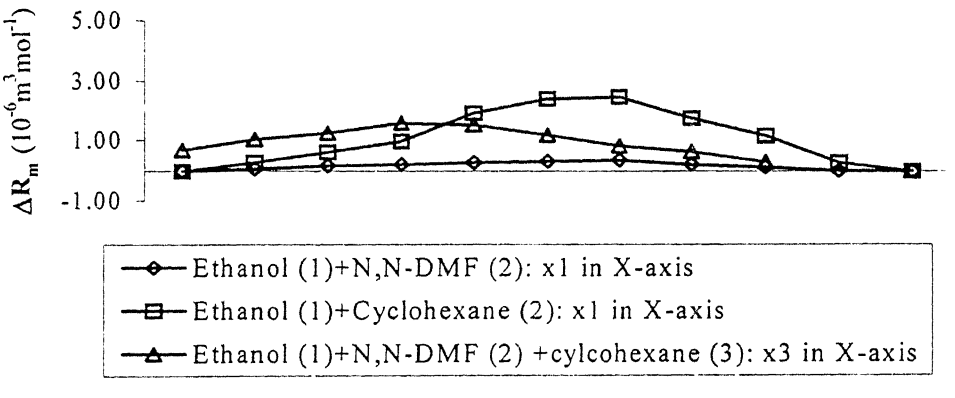


Fig. 2. (b): Deviations in molar refractivity (ΔR_m) in binary and ternary liquid mixtures



CHAPTER – 5

Estimation of molecular radii of liquids and liquid mixtures from sound velocity

Molecular radius is one of the parameters of pure liquids and liquid mixtures, which reflects their structural features. Liquids in their mixtures behave differently than they behave individually. Relative strength of A-B interaction is different in different mixtures. When a particular liquid molecule is enforced to interact with another molecule in mixture, it may or may not have same shape as it has in pure liquids. Molecular radius is thus not only related to the number of atoms involved but also with the nature of liquids.

Molecular radius is, directly or indirectly, an important parameter in the theories of liquids like Collision Factor Theory (CFT)[1-2] and Scaled Particle Theory[3-4]. Molecular radius has been utilized to evaluate some other important properties of liquids[5-6]. Surface tension or viscosity has been utilised for the computation of molecular diameter/ radius by some workers[7-10]. Ultrasonic techniques are the most powerful tools for the structural and physico-chemical studies of the liquids[11]. Ultrasonic velocity and density data can be utilized to estimate the molecular radius in pure liquids and liquid mixtures. The effects of various parameters on molecular radius in pure liquids have been studied earlier[12], using various acoustic methods suggested by Schaaffs[1,13], Rao[14], Eyring[15-16] and Kittel[17]. Along with these acoustic methods, the relation based upon the assumption that liquid system is made up of closely packed molecules with face centered cubic structures, has also been employed[12]. The results obtained from these acoustic methods can be utilized to compute various other parameters and can be related with velocity of sound in liquids. It is observed that the velocity of sound in a liquid is five to ten times higher than in their saturated vapours. This difference in the results of sound velocity is due to decreased intermolecular distance in liquids[18].

To the best of our knowledge, various methods of determining molecular radius of liquid mixtures have not been analysed by the previous workers. The studies on these relations for pure liquids also, are not sufficient to provide idea about the variation of

molecular radius in a homologous series. In the present work, the acoustic methods for estimating molecular radius have been employed in various organic liquids and liquid mixtures. Molecular radius can also be computed using refractive index and density data[19]. An attempt has also been made to compare the values obtained from the acoustic methods with the values obtained from refractive index method. The values obtained from refractive index method have been taken as the reference or experimental ones, the concept being used elsewhere[12] also. The contributing parameters have been co-related with molecular radius. The deviations in variation patterns of molecular radii with changing temperature, pressure and mole fraction of a particular type of the component of the mixture have also been studied.

5.2 Theoretical

A number of relations, eqs (1) – (4), can be employed to estimate the molecular radius in liquids using sound velocity and related data. Out of which, Schaaffs and Rao methods are based upon van der Waals equation of state. Kittel and Eyring methods are based upon the assumption that observed velocity of sound results from the propagation of sound waves inside the molecule and in the free space between them. These acoustic methods for the determination of molecular radius are summarised here.

Schaaffs Relation

$$r = \sqrt[3]{\frac{M}{\rho N}}\sqrt[3]{\frac{3}{16\pi}\left[1-\frac{\gamma RT}{Mu^2}\left(\sqrt{1+\frac{Mu^2}{3\gamma RT}}-1\right)\right]} \qquad ...(1)$$

Rao's Relation

$$r = \sqrt[3]{\frac{M}{\rho N}}\sqrt[3]{\frac{3}{16\pi}\left[1-\frac{\gamma RT}{Mu^2}\left(\sqrt{1+\frac{Mu^2}{\gamma RT}}-1\right)\right]} \qquad ...(2)$$

Eyring's Relation

$$r = \sqrt[3]{\frac{M}{\rho N}}\frac{1}{2}\sqrt[3]{\left[1-\left(1-\frac{1}{u}\sqrt{\frac{\gamma RT}{M}}\right)^{3}\right]\sqrt{2}} \qquad ...(3)$$

Kittels's Relation

$$r = \sqrt[3]{\frac{M}{\rho N}}\frac{1}{2}\sqrt[3]{\left(1-\frac{1}{u}\sqrt{\frac{3\gamma RT}{M}}\right)\sqrt{2}} \qquad ...(4)$$

In all these relations,

N= Avogadro's number ρ = density u = sound velocity

M = molecular mass γ= specific heat ratio.

Besides acoustic methods, for a system made-up of spheres with mass M/N in a close-packed face-centered cubic structure (CP-FCC), molecular radius can also be obtained from the relation[12]

$$r = \frac{1}{2}\sqrt[3]{\frac{M\sqrt{2}}{\rho N}} \qquad ...(5)$$

This equation is based upon the assumption that there is no free space between the spheres (molecules). The values of molecular radius obtained from any other method must always be lower than the values obtained from this method. Refractive index data can be utilized in conjunction with molar volume to compute molecular radius using the following relation[19]:

$$r = \left[\frac{3}{4\pi N}\frac{n^2-1}{n^2+2}V_m\right]^{\frac{1}{3}} \qquad ...(6)$$

This relation provides non-acoustic method for the estimation of molecular radius.

Molar mass of liquid mixtures can be obtained from the molar masses of pure liquid components using the relation, $M_{mix}=\sum M_i x_i$, where M_i and x_i are the molecular mass and the mole fraction of the component of liquid mixture.

5.3 Results and Discussion

The molecular radii of various organic liquids and liquid mixtures at various conditions of temperature and pressure have been computed using eqs (1) – (6). Sound velocity and related data required for the calculation of molecular radius have been taken from the various sources[21-28]. The calculated values of molecular radius for various pure liquids and liquid mixtures have been presented in tables 1-12. The graphical representations of some important results have been displayed in figures 1-6.

As far as experimental results are concerned, no such significant change in molecular radii with changing temperature has been observed (figures 1-2 and tables 1-11). Though results from Rao method show regular trend of change in molecular radii with changing temperature, there is a bit high departure in values from the experimental values (figures 1-2, figures 5-6 and tables 1-11). This departure can be explained in terms of difference of only one term in the relation given by Shaaffs and Rao, eqs (1) and (2). The values of molecular radius obtained from Eyring and Kittel relations have been not found to be in agreement with the experimental values (figures 1-2, figures 5-6 and tables 1-11). These results show that the idea of free space between molecules has to be reconsidered. These relations need several modifications in the present cases. The values of molecular radius obtained from eq (5) are always found to be higher than the values obtained from any other method. This result is obvious, as this equation is based upon the assumption that there is no free space between the spheres (molecules). The application of this equation for any liquid systems should only be limited to estimate the maximum possible values of molecular radius, if molecules are assumed spheres and there is no free space between molecules. Schaaffs method has been found to give the best results as

compared with the experimental results (figures 1-2, figures 5-6 and tables 1-11). The benefit of using Schaaffs method is not only its applicability but also the need of minimum easily measurable data like ultrasonic velocity, density and specific heat ratio. In the case where specific heat ratio is not available, the equation can be simplified by neglecting the γ term without significant differences[5,6]. There is a regular increase of molecular radius in the case of the members of homologous series (alkanes are taken is present case). This fact seems to be obvious and has a regular trend also (figures 3-4). It is also interesting to note that, though Schaaffs method gives slight deviations from experimental results in case of higher members, deviation pattern is constant and not tangible.

Tables 6-8 and figure-6 show the applicability of Schaaffs method for the calculation of molecular radius for binary liquid mixtures. The values of molecular radius obtained in the case of liquid mixtures show that Schaaffs method provides best results in these cases. The regular decrease in molecular radius with increasing mole fraction of ethyl acetate (figure 6) also seems to be obvious as ethyl acetate has lower molecular radius than cyclohexane. Regular and slight decrease in molecular radius of methane with increasing pressure is observed (figure 4) in all the methods except Kittel method, which seems to be logical and obvious.

The acoustic methods for the determination of molecular radius are found to be very suitable for ***pure liquids*** as well as for ***liquid mixtures***. The increase in molecular radius in the higher homologues is found to be very convincing and logical. The variation pattern of molecular radius with the change in various parameters of liquids and liquid mixtures seem to be very convincing. The Schaaffs method seems to be applicable for ***pure liquids*** as well as for ***liquid mixtures*** also. This relation can, thus, be utilized to estimate the variety of other parameters of liquids and liquid mixtures.

5.4 References

1. Schaaffs W, *Z Physik*, **114** (1939) 110.

2. Kaulgad M V, *Z Physik Chemie (Leipig)*, **36** (1963) 365.
3. Reiss H, Frisch H L & Lebowitz J L, *J Chem Phys*, **31** (1959) 369.
4. Lebowitz J L, Helfand E & Praestgraad E, *J Chem Phys*, **43** (1965) 77.
5. Mishra R L & Pandey J D, *Ind J Pure Appl Phys*, **15(7)** (1977) 505.
6. Pandey J D & Gupta U, *Electrochim Acta*, **28(8)** (1983) 1047.
7. Chaturvedi C V & Pratap S, *Acustica*, **42** (1979) 260.
8. Pandey J D & Mishra K, *Acoustics Letters*, **6(10)** (1983) 148.
9. Pant N, Chaturvedi C V & Chaturvedi G D, *Z Phys Chemie (Leipig)*, **264** (1983) 3.
10. Mason E A & Monachiek, *J Chem Phys*, **35** (1961) 1676.
11. Settle D, "Study of simple liquids by ultrasonic methods", Chapter IX in "*Physics of simple liquids*", Temperley H N V, Rowlinson J S and Ruhbrooke G S; North Holland Publishing Company, Amsterdam, 1968.
12. Ernst E & Glinski J, *Acustica*, **13** (1981) 109.
13. Schaaffs W, *Acustica*, **33** (1975) 272.
14. GopalaRao R V & Venkataseshaiah V, *Z Phys Chem*, **242** (1969) 193.
15. Kincaid J F & Eyring H, *J Chem Phys*, **5** (1937) 587.
16. Kincaid J F & Eyring H, *J Chem Phys*, **6**(1938 620.
17. Kittel C, *J Chem Phys*, **14** (1946) 614.
18. Bhatia A B, *Ultrasonic Absorption*, Clerendon Press, Oxford, 1967.
19. Glasstone S, *Textbook of physical chemistry*, London, MacMillan & Co Ltd, 1962.
20. Low D I R & Moelwyn-Hughes E A, *Proc Roy Soc*, **267** (1962) 384.
21. Singer J R, *J Chem Phys*, **51** (1969) 4729.
22. Oswal S L & Palsanawala P P, *Acoustic Letters*, **13** (1989) 66.
23. Aminabhavi T M & Gopalkrishna B, *J Chem Eng Data*, **39** (1994) 529.
24. Aminabhavi T M et al, *J Chem Eng Data*, **39** (1994) 522.
25. Rajendran V, *Ind J Pure & Appl Phys*, **32** (1994) 19.

Table - 1

Molecular radii of Alkanes

T	ρ	u	*n*	r (10^{-9} m)					
K	*kg m^{-3}*	*m s^{-1}*		*Eq (1)*	*Eq (2)*	*Eq (3)*	*Eq (4)*	*Eq (5)*	*Eq (6)*
Hexane									
298.15	661.2	1074	1.3755	0.2280	0.2211	0.2642	0.2728	0.3369	0.2278
303.15	656.7	1051	1.3731	0.2284	0.2213	0.2668	0.2721	0.3376	0.2279
308.15	651.8	1025	1.3707	0.2289	0.2215	0.2696	0.2713	0.3385	0.2280
313.15	647.3	1001	1.3672	0.2292	0.2217	0.2723	0.2703	0.3393	0.2279
318.15	642.4	980	1.3642	0.2297	0.2219	0.2748	0.2696	0.3401	0.2279
Heptane									
298.15	679.3	1137	1.3857	0.2383	0.2320	0.2655	0.2905	0.3510	0.2393
303.15	675.0	1117	1.3828	0.2387	0.2323	0.2677	0.2901	0.3518	0.2393
308.15	670.6	1090	1.3805	0.2391	0.2324	0.2705	0.2894	0.3526	0.2394
313.15	666.3	1073	1.3782	0.2395	0.2327	0.2726	0.2891	0.3533	0.2395
318.15	661.8	1059	1.3761	0.2399	0.2330	0.2746	0.2889	0.3541	0.2396
Octane									
298.15	698.4	1172	1.3956	0.2471	0.2412	0.2672	0.3046	0.3633	0.2496
303.15	694.3	1156	1.3929	0.2475	0.2415	0.2692	0.3045	0.3640	0.2495
308.15	690.2	1137	1.3906	0.2478	0.2417	0.2714	0.3042	0.3647	0.2496
313.15	686.2	1116	1.3880	0.2482	0.2419	0.2737	0.3038	0.3655	0.2496
318.15	682.0	1096	1.3855	0.2486	0.2422	0.2761	0.3035	0.3662	0.2496
Nonane									
298.15	714.5	1209	1.4034	0.2553	0.2498	0.2686	0.3176	0.3748	0.2589
303.15	706.8	1166	1.3989	0.2560	0.2502	0.2731	0.3171	0.3761	0.2590
308.15	699.0	1126	1.3938	0.2567	0.2507	0.2777	0.3166	0.3775	0.2590
Decane									
298.15	726.5	1239	1.4101	0.2632	0.2580	0.2703	0.3297	0.3858	0.2678
303.15	718.9	1190	1.4055	0.2639	0.2584	0.2752	0.3291	0.3872	0.2679
308.15	711.4	1158	1.4009	0.2646	0.2589	0.2792	0.3289	0.3885	0.2679
Dodecane									
298.15	746.1	1282	1.4192	0.2775	0.2727	0.2740	0.3510	0.4061	0.2837
303.15	738.6	1241	1.4161	0.2783	0.2733	0.2785	0.3509	0.4074	0.2840
308.15	731.4	1207	1.4114	0.2790	0.2738	0.2825	0.3508	0.4088	0.2840
Tetradecane									
298.15	760.8	1317	1.4270	0.2906	0.2861	0.2776	0.3700	0.4245	0.2982
303.15	753.6	1278	1.4231	0.2913	0.2866	0.2819	0.3700	0.4258	0.2983
308.15	746.4	1241	1.4190	0.2921	0.2872	0.2861	0.3700	0.4272	0.2984

Table - 2

Molecular radius of Acetone

T	ρ	u	γ	r (10^{-9} m)				
K	*kg m^{-3}*	*m s^{-1}*		*Eq (1)*	*Eq (2)*	*Eq (3)*	*Eq (4)*	*Eq (5)*
253.20	833.9	1365	1.405	0.1857	0.1810	0.2045	0.2274	0.2734
263.20	823.0	1321	1.396	0.1863	0.1814	0.2081	0.2269	0.2746
273.20	812.1	1275	1.398	0.1870	0.1817	0.2121	0.2261	0.2758
283.20	801.0	1230	1.385	0.1876	0.1821	0.2160	0.2253	0.2771
293.20	790.0	1185	1.375	0.1883	0.1825	0.2199	0.2244	0.2784
303.20	778.9	1140	1.363	0.1890	0.1828	0.2239	0.2233	0.2797
308.20	773.3	1117	1.362	0.1894	0.1830	0.2261	0.2225	0.2803

Table - 3

Molecular radius of Methane

T	P×10^{-4}	ρ	u	γ	r (10^{-9} m)				
K	*N m^{-2}*	*kg m^{-3}*	*m s^{-1}*		*Eq (1)*	*Eq (2)*	*Eq (3)*	*Eq (4)*	*Eq (5)*
145.60	8.8	372.0	970	2.24	0.1556	0.1457	0.2177	0.1502	0.2336
145.60	18.6	374.0	980	2.27	0.1552	0.1454	0.2169	0.1503	0.2330
145.60	31.2	378.0	1020	2.29	0.1551	0.1455	0.2152	0.1547	0.2326
145.60	51.2	382.0	1050	2.28	0.1546	0.1454	0.2132	0.1578	0.2317
145.60	73.5	385.0	1080	2.20	0.1542	0.1454	0.2106	0.1622	0.2309
145.60	87.5	400.0	1100	2.07	0.1540	0.1455	0.2081	0.1665	0.2303
125.00	3.5	403.0	1200	1.93	0.1526	0.1457	0.1969	0.1792	0.2274
125.10	10.4	406.0	1210	1.88	0.1523	0.1456	0.1955	0.1801	0.2269
125.00	36.1	409.0	1240	1.78	0.1521	0.1457	0.1927	0.1826	0.2263
124.90	60.0	412.0	1260	1.76	0.1518	0.1456	0.1912	0.1834	0.2257
125.00	81.0	413.0	1282	1.78	0.1515	0.1453	0.1902	0.1835	0.2252
125.10	89.1	420.0	1295	1.79	0.1514	0.1453	0.1898	0.1837	0.2250
113.00	2.4	420.0	1330	1.78	0.1508	0.1452	0.1851	0.1865	0.2237
113.60	7.9	420.0	1332	1.79	0.1508	0.1451	0.1852	0.1864	0.2237
114.00	14.1	420.0	1335	1.80	0.1508	0.1451	0.1853	0.1863	0.2237
115.00	27.0	420.0	1340	1.81	0.1508	0.1451	0.1855	0.1861	0.2237
117.00	52.0	421.0	1345	1.83	0.1507	0.1450	0.1860	0.1856	0.2237
112.00	1.7	424.0	1350	1.76	0.1508	0.1453	0.1838	0.1875	0.2236
111.90	30.8	427.0	1380	1.75	0.1505	0.1451	0.1822	0.1881	0.2230
112.10	62.5	430.0	1400	1.73	0.1502	0.1450	0.1809	0.1885	0.2225
112.00	89.0	438.0	1430	1.74	0.1499	0.1448	0.1796	0.1888	0.2220
105.00	1.7	450.0	1485	1.72	0.1492	0.1445	0.1751	0.1905	0.2206
94.00	1.7	0.450	1520	1.69	0.1481	0.1439	0.1695	0.1916	0.2187

Table – 4

Molecular radius of Diglyme

T	ρ	u	n	r (10^{-9} m)					
K	*kg m^{-3}*	*m s^{-1}*		*Eq (1)*	*Eq (2)*	*Eq (3)*	*Eq (4)*	*Eq (5)*	*Eq (6)*
298.15	939.9	1284	1.4058	0.2371	0.2326	0.2398	0.2981	0.3473	0.2403
303.15	935.6	1266	1.4040	0.2373	0.2328	0.2415	0.2980	0.3478	0.2404
308.15	930.1	1250	1.4017	0.2377	0.2331	0.2433	0.2981	0.3485	0.2404
313.15	925.7	1229	1.3992	0.2380	0.2333	0.2453	0.2979	0.3490	0.2404
318.15	920.1	1203	1.3972	0.2384	0.2335	0.2476	0 2977	0.3497	0.2405

Table – 5

Molecular radius of Methyl iodide

T	ρ	u	γ	r (10^{-9} m)				
K	*kg m^{-3}*	*m s^{-1}*		*Eq (1)*	*Eq (2)*	*Eq (3)*	*Eq (4)*	*Eq (5)*
253.20	2389.3	944	1.534	0.1762	0.1720	0.1921	0.2167	0.2593
263.20	2361.5	918	1.544	0.1768	0.1722	0.1956	0.2161	0.2603
273.20	2333.5	892	1.551	0.1773	0.1725	0.1990	0.2154	0.2613
283.20	2305.5	866	1.548	0.1779	0.1728	0.2024	0.2148	0.2624
293.20	2277.3	840	1.544	0.1784	0.1731	0.2057	0.2140	0.2635
303.20	2249.2	814	1.527	0.1790	0.1735	0.2089	0.2133	0.2646
308.20	2235.4	801	1.516	0.1793	0.1736	0.2105	0.2130	0.2651

Table – 6

Molecular radius of binary liquid mixture: Cyclohexane (1) + Benzene (2)

T	x_1	ρ	u	n	r (10^{-9} m)					
K		*kg m^{-3}*	*m s^{-1}*		*Eq (1)*	*Eq (2)*	*Eq (3)*	*Eq (4)*	*Eq (5)*	*Eq (6)*
303.15	0.0000	868.5	1276	1.4945	0.2021	0.1970	0.2234	0.2472	0.2977	0.2181
	0.1980	842.0	1253	1.4767	0.2052	0.1999	0.2279	0.2505	0.3023	0.2192
	0.4000	818.6	1238	1.4581	0.2082	0.2027	0.2318	0.2539	0.3067	0.2199
	0.5005	808.6	1231	1.4504	0.2096	0.2040	0.2336	0.2554	0.3087	0.2202
	0.6040	799.3	1228	1.4423	0.2109	0.2054	0.2351	0.2570	0.3107	0.2205
	0.7996	783.1	1225	1.4311	0.2134	0.2078	0.2378	0.2601	0.3144	0.2214
	1.0000	769.1	1228	1.4208	0.2157	0.2101	0.2399	0.2632	0.3178	0.2223
323.15	0.0000	846.7	1180	1.4816	0.2035	0.1977	0.2315	0.2457	0.3002	0.2183
	0.1980	821.4	1155	1.4623	0.2065	0.2006	0.2363	0.2487	0.3048	0.2191
	0.4000	798.2	1142	1.4456	0.2095	0.2034	0.2403	0.2520	0.3093	0.2200
	0.5005	788.4	1136	1.4382	0.2109	0.2048	0.2421	0.2536	0.3114	0.2204
	0.6040	779.2	1133	1.4370	0.2123	0.2061	0.2437	0.2552	0.3134	0.2216
	0.7996	763.5	1127	1.4200	0.2147	0.2085	0.2467	0.2581	0.3170	0.2216
	1.0000	749.6	1130	1.4099	0.2171	0.2108	0.2489	0.2612	0.3205	0.2225

Table – 7

Molecular radius of binary liquid mixture: Diglyme(1)+Hexane(2)

T	x_1	ρ	u	n	r (10^{-9} m)					
K		*kg m^{-3}*	*m s^{-1}*		*Eq (1)*	*Eq (2)*	*Eq (3)*	*Eq (4)*	*Eq (5)*	*Eq (6)*
298.15	0.1017	690.3	1082	1.3782	0.2291	0.2225	0.2624	0.2759	0.3382	0.2292
	0.2006	718.7	1098	1.3810	0.2302	0.2238	0.2600	0.2789	0.3394	0.2306
	0.3006	748.0	1115	1.3838	0.2311	0.2250	0.2575	0.2816	0.3404	0.2317
	0.3974	775.2	1138	1.3869	0.2320	0.2262	0.2549	0.2844	0.3415	0.2330
	0.4984	804.0	1153	1.3909	0.2328	0.2273	0.2527	0.2868	0.3425	0.2344
	0.5986	832.2	1179	1.3938	0.2337	0.2284	0.2499	0.2893	0.3434	0.2356
	0.6954	858.8	1203	1.3968	0.2345	0.2294	0.2474	0.2916	0.3444	0.2367
	0.8011	887.8	1236	1.4013	0.2354	0.2306	0.2444	0.2940	0.3453	0.2382
	0.8957	913.7	1261	1.4036	0.2361	0.2315	0.2419	0.2960	0.3461	0.2392
303.15	0.1017	685.7	1066	1.3753	0.2296	0.2228	0.2644	0.2755	0.3390	0.2292
	0.2006	713.9	1082	1.3786	0.2306	0.2241	0.2620	0.2786	0.3402	0.2306
	0.3006	743.2	1098	1.3814	0.2315	0.2253	0.2596	0.2814	0.3412	0.2318
	0.3974	770.4	1117	1.3848	0.2324	0.2264	0.2571	0.2841	0.3422	0.2331
	0.4984	798.9	1135	1.3886	0.2332	0.2275	0.2547	0.2866	0.3432	0.2345
	0.5986	827.3	1159	1.3911	0.2341	0.2286	0.2520	0.2891	0.3441	0.2356
	0.6954	853.9	1182	1.3944	0.2349	0.2297	0.2495	0.2914	0.3450	0.2368
	0.8011	882.9	1214	1.3978	0.2357	0.2308	0.2465	0.2939	0.3460	0.2380
	0.8957	908.8	1239	1.4012	0.2365	0.2317	0.2440	0.2958	0.3468	0.2392
308.15	0.1017	680.8	1040	1.3728	0.2300	0.2230	0.2672	0.2748	0.3398	0.2293
	0.2006	709.1	1054	1.3759	0.2310	0.2242	0.2649	0.2778	0.3409	0.2307
	0.3006	738.3	1075	1.3790	0.2319	0.2255	0.2620	0.2809	0.3419	0.2319
	0.3974	765.4	1096	1.3832	0.2328	0.2267	0.2594	0.2837	0.3429	0.2334
	0.4984	794.2	1114	1.3863	0.2336	0.2277	0.2569	0.2862	0.3439	0.2345
	0.5986	822.3	1136	1.3889	0.2344	0.2288	0.2543	0.2887	0.3448	0.2356
	0.6954	849.0	1166	1.3920	0.2352	0.2299	0.2513	0.2913	0.3457	0.2368
	0.8011	877.8	1193	1.3960	0.2361	0.2310	0.2486	0.2937	0.3466	0.2382
	0.8957	903.9	1218	1.3993	0.2368	0.2319	0.2460	0.2957	0.3474	0.2393
313.15	0.1017	676.1	1018	1.3698	0.2304	0.2232	0.2697	0.2741	0.3406	0.2293
	0.2006	704.5	1035	1.3730	0.2314	0.2245	0.2671	0.2773	0.3417	0.2306
	0.3006	733.6	1053	1.3766	0.2322	0.2256	0.2644	0.2803	0.3426	0.2319
	0.3974	760.3	1073	1.3802	0.2332	0.2269	0.2619	0.2832	0.3437	0.2333
	0.4984	789.5	1092	1.3838	0.2340	0.2279	0.2593	0.2858	0.3446	0.2346
	0.5986	817.6	1116	1.3864	0.2348	0.2290	0.2564	0.2884	0.3455	0.2356
	0.6954	844.2	1144	1.3904	0.2356	0.2301	0.2536	0.2910	0.3463	0.2370
	0.8011	873.0	1172	1.3936	0.2364	0.2312	0.2506	0.2935	0.3473	0.2382
	0.8957	889.1	1199	1.3971	0.2380	0.2330	0.2490	0.2966	0.3493	0.2402

Table – 8

Molecular radius of binary liquid mixture: Ethyl acetate (1) + Cyclohexane (2)

T	x_1	ρ	u	n	r (10^{-9} m)					
K		*kg m^{-3}*	*m s^{-1}*		*Eq (1)*	*Eq (2)*	*Eq (3)*	*Eq (4)*	*Eq (5)*	*Eq (6)*
303.15	0.0000	769.1	1228	1.4208	0.2157	0.2101	0.2399	0.2632	0.3178	0.2223
	0.1013	777.8	1206	1.4140	0.2152	0.2095	0.2403	0.2621	0.3171	0.2207
	0.2021	786.5	1184	1.4079	0.2147	0.2089	0.2407	0.2610	0.3164	0.2193
	0.3020	795.6	1167	1.4023	0.2142	0.2083	0.2408	0.2600	0.3157	0.2179
	0.4007	805.4	1155	1.3924	0.2136	0.2078	0.2406	0.2591	0.3149	0.2158
	0.4985	816.0	1143	1.3907	0.2129	0.2071	0.2403	0.2581	0.3140	0.2149
	0.5994	828.2	1134	1.3851	0.2122	0.2064	0.2397	0.2571	0.3129	0.2132
	0.6952	841.0	1126	1.3802	0.2114	0.2056	0.2390	0.2561	0.3118	0.2117
	0.8001	856.3	1123	1.3757	0.2105	0.2047	0.2378	0.2551	0.3104	0.2100
	0.8998	872.0	1124	1.3720	0.2096	0.2038	0.2363	0.2542	0.3090	0.2084
	1.0000	888.5	1118	1.3673	0.2086	0.2029	0.2352	0.2530	0.3076	0.2066
323.15	0.0000	749.6	1130	1.4099	0.2171	0.2108	0.2489	0.2612	0.3205	0.2225
	0.1013	755.3	1110	1.4034	0.2169	0.2105	0.2497	0.2604	0.3202	0.2212
	0.2021	763.6	1094	1.3969	0.2164	0.2099	0.2498	0.2594	0.3196	0.2197
	0.3020	773.6	1069	1.3913	0.2157	0.2091	0.2504	0.2578	0.3187	0.2182
	0.4007	784.4	1056	1.3856	0.2150	0.2084	0.2501	0.2567	0.3177	0.2166
	0.4985	795.7	1049	1.3790	0.2143	0.2077	0.2494	0.2558	0.3166	0.2148
	0.5994	807.7	1038	1.3747	0.2135	0.2069	0.2489	0.2546	0.3156	0.2133
	0.6952	819.4	1034	1.3696	0.2128	0.2063	0.2480	0.2538	0.3145	0.2117
	0.8001	832.9	1032	1.3658	0.2120	0.2055	0.2469	0.2530	0.3133	0.2103
	0.8998	847.3	1028	1.3612	0.2111	0.2047	0.2458	0.2520	0.3120	0.2086
	1.0000	863.7	1025	1.3573	0.2101	0.2037	0.2444	0.2509	0.3105	0.2069

Table – 9

Molecular radius of ternary liquid mixture:

1-Benzene (1) + Chloroform (2) + Cyclohexane (3)

T	x_1	x_2	ρ	u	r (10^{-9} m)				
K			*kg m^{-3}*	*m s^{-1}*	*Eq (1)*	*Eq (2)*	*Eq (3)*	*Eq (4)*	*Eq (5)*
303 15	0.1015	0.3019	945.3	1125	0.2091	0.2037	0.2324	0.2552	0.3081
	0.2019	0.2990	957.4	1122	0.2077	0.2023	0.2311	0.2534	0.3060
	0.2998	0.2993	965.6	1129	0.2067	0.2013	0.2297	0.2523	0.3045
	0.4001	0.3002	981.3	1134	0.2052	0.1999	0.2277	0.2506	0.3022
	0.5045	0.2983	996.3	1142	0.2037	0.1984	0.2256	0.2489	0.3000
	0.6031	0.2976	1011.9	1146	0.2022	0.1970	0.2238	0.2471	0.2977

Table – 10

Molecular radius of ternary liquid mixture:

Toluene (1) +Chloroform (3) + Cyclohexane (3)

T	x_1	x_2	ρ	u	r (10^{-9} m)				
K			*kg m^{-3}*	*m s^{-1}*	*Eq (1)*	*Eq (2)*	*Eq (3)*	*Eq (4)*	*Eq (5)*
303.15	0.0911	0.3685	981.5	1106	0.2092	0.2039	0.2319	0.2556	0.3082
	0.2198	0.2939	947.8	1134	0.2106	0.2052	0.2326	0.2576	0.3101
	0.3004	0.3036	962.7	1143	0.2102	0.2050	0.2312	0.2576	0.3095
	0.4013	0.3026	969.1	1145	0.2104	0.2051	0.2309	0.2580	0.3096
	0.5016	0.2999	981.3	1152	0.2100	0.2049	0.2297	0.2579	0.3091
	0.5976	0.3035	994.8	1159	0.2098	0.2047	0.2286	0.2579	0.3086

Table – 11

Molecular radius of ternary liquid mixture:

Chlorobenzene (1) + Chloroform (2) + Cyclohexane (3)

T	x_1	x_3	ρ	u	r (10^{-9} m)				
K			*kg m^{-3}*	*m s^{-1}*	*Eq (1)*	*Eq (2)*	*Eq (3)*	*Eq (4)*	*Eq (5)*
303.15	0.1001	0.5965	965.9	1126	0.2103	0.2050	0.2321	0.2573	0.3096
	0.1988	0.4978	999.8	1132	0.2100	0.2048	0.2300	0.2577	0.3090
	0.3150	0.3975	1032.6	1141	0.2097	0.2046	0.2279	0.2581	0.3084
	0.4005	0.3001	1076.8	1142	0.2087	0.2038	0.2255	0.2575	0.3069
	0.5023	0.1995	1111.6	1151	0.2085	0.2037	0.2234	0.2579	0.3064
	0.5997	0.0996	1148.8	1156	0.2081	0.2034	0.2214	0.2580	0.3057

Fig. 1: Molecular radius of hexane at varying temperature calculated using various relations

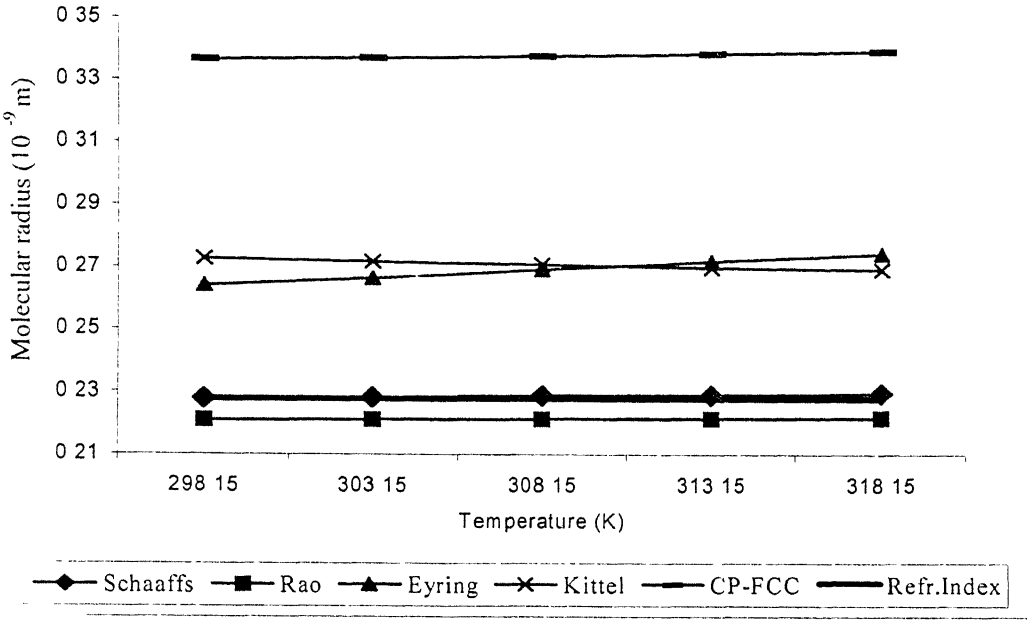


Fig. 2: Molecular radius of octane at varying temperature calculated using various relations

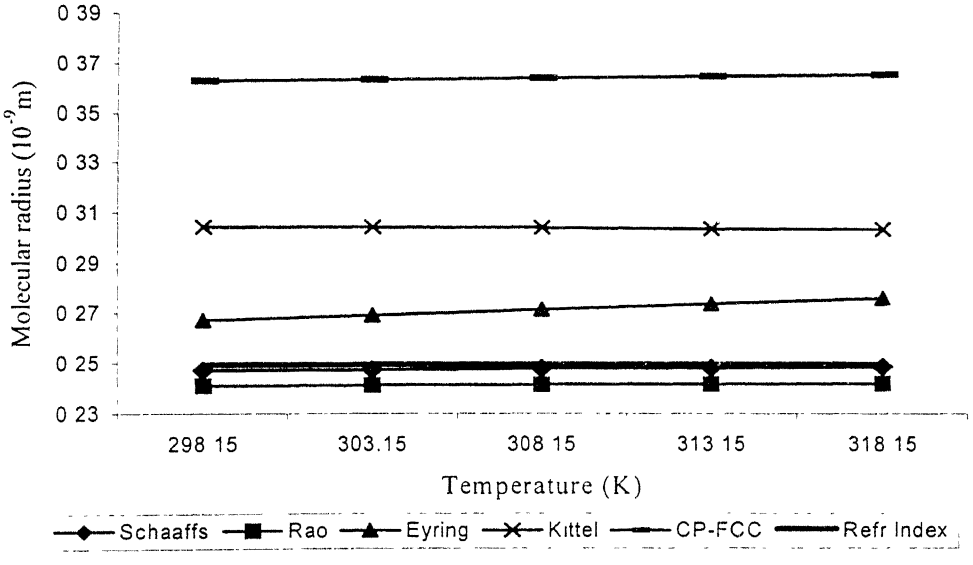


Fig. 3: Molecular radii of various alkanes at 298.15K

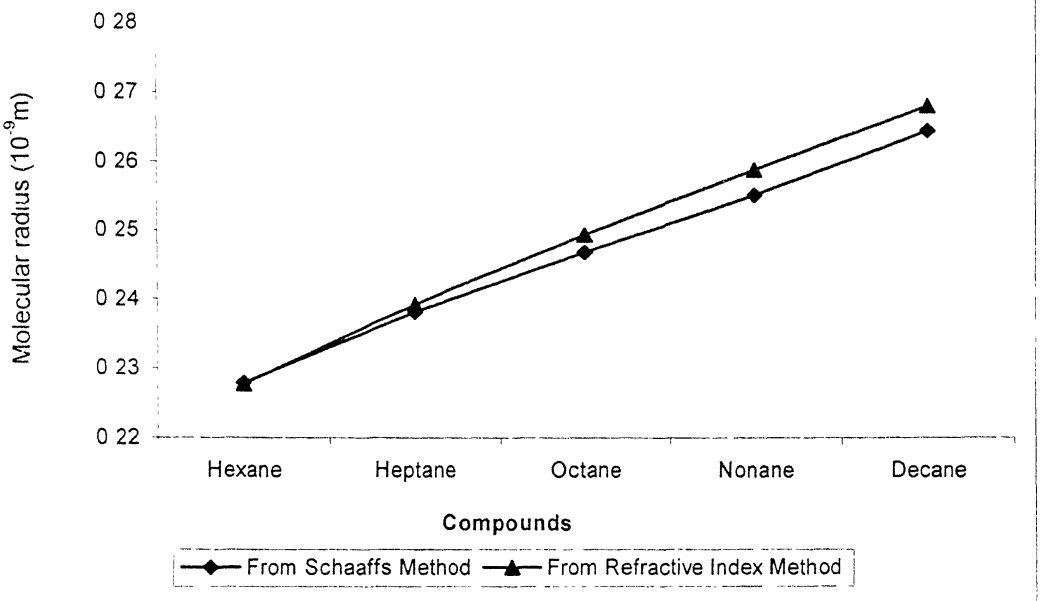


Fig. 4: Molecular radii of various alkanes at 308.15K

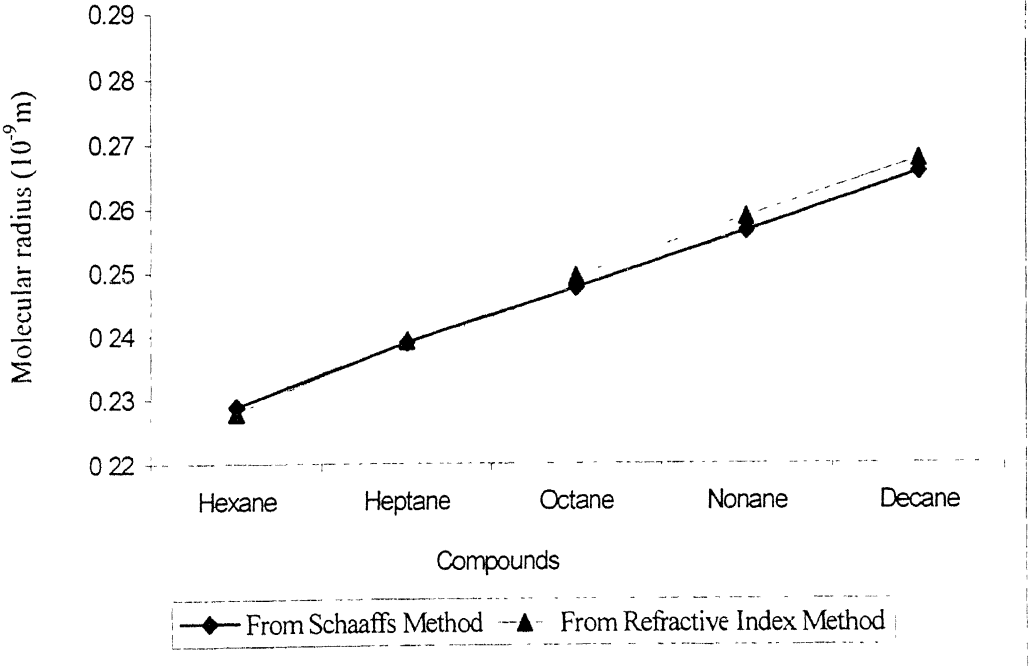


Fig. 5: Molecular radius of methane at different pressures at 145.6 K

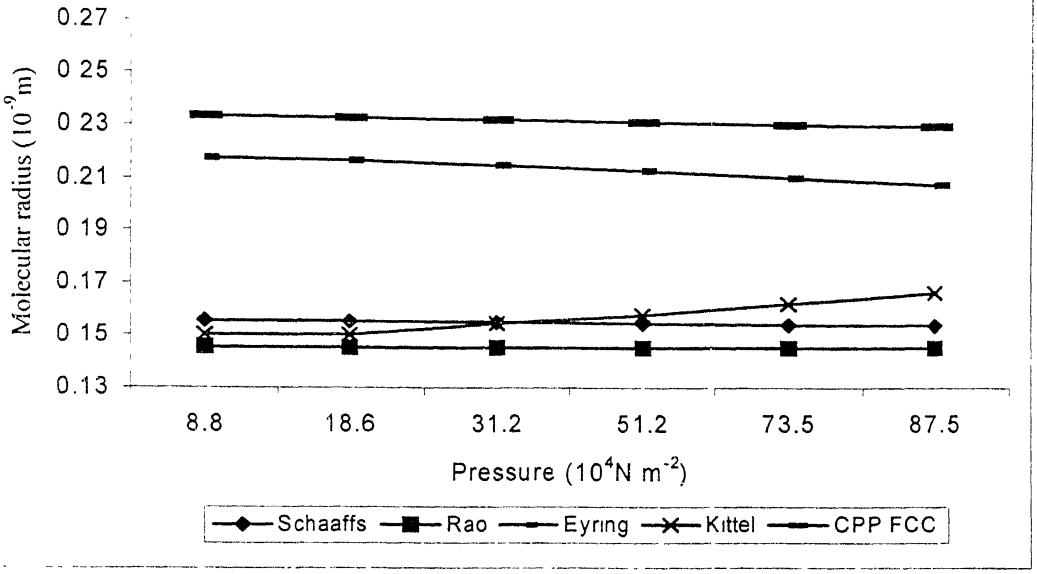
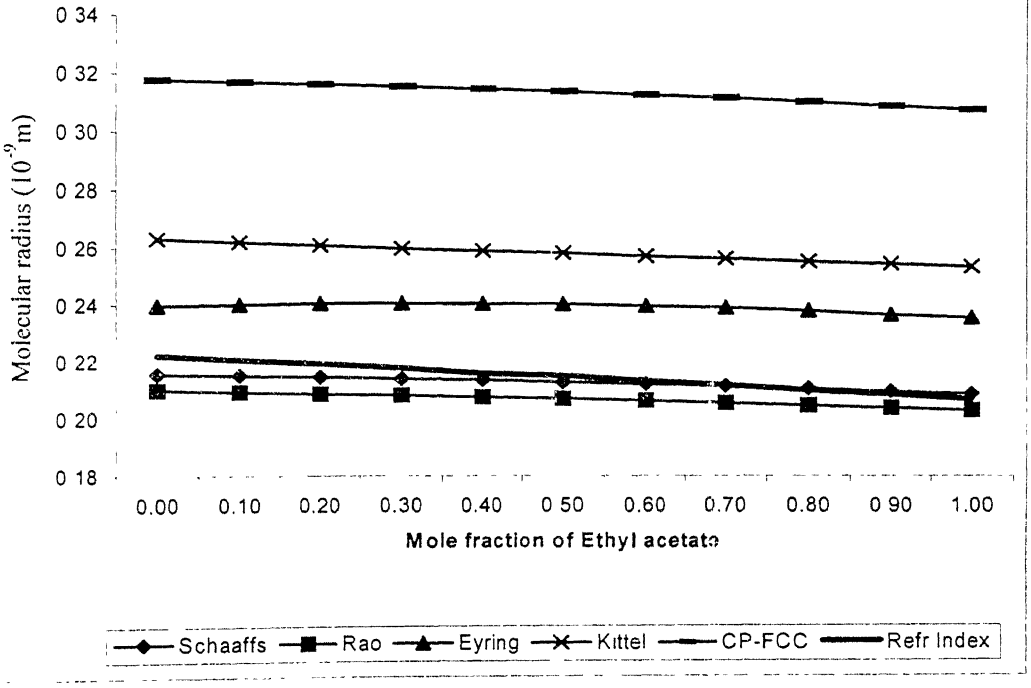


Fig. 6: Molecular radius of binary mixture: Ethyl acetate(1)+Cyclohexane at 303.15 K



CHAPTER – 6

Internal pressure and related properties of liquids and liquid mixtures

Internal pressure is a fundamental liquid property, which is a resultant of forces of attraction and repulsion between the constituents of liquids. As degree of cohesion differs from liquids to liquids, internal pressure provides useful information about the molecular interactions in the liquid systems. Internal pressure is zero for ideal gases as molecular forces are absent. But in imperfect gases and liquids, internal pressure is appreciable. Richards[1], Dack[2] and Hildebrand & Scott[3-4] recognised the importance of this property of liquids. Internal pressure has gained enormous amount of interest by chemists, physicists and chemical engineers in recent past, as it provides a measure of explaining molecular interactions, internal structure, clustering phenomenon, ionic interactions, dipolar interactions and surface tension. Various relations for the estimation of internal pressure in liquids have been proposed[5-10]. Studies by some workers[11-16] on the various other parameters of liquids have turned to be very useful in the extension of the studies on internal pressure. Barton[17,18] explained extensively about the internal pressure and its related parameters of liquid state. Internal pressure and related parameters in liquids and liquid mixtures have been evaluated by various workers[19-31], using various relations. Renuncio et al[19] utilised density data of some organic liquids to evaluate internal pressure and compared the values with solubility parameter. Pandey and Mishra[20] evaluated excess internal pressure in some organic liquid mixtures and utilised the values to study molecular interactions. Sharma[9] studied the relationship between internal pressure and cohesive energy density in liquids and described the molecular interactions in terms of pseudo-Gruneisen parameter of liquid state. Pandey[21] evaluated excess internal pressure in various liquid mixtures with the aid of surface tension data computed using Flory statistical theory[21]. Pandey et al[22] evaluated excess internal pressure in organic liquids mixtures using Buehler et al[5,6] method in conjunction with hard-sphere model. Buehler et al[5,6] method for evaluation of internal pressure was also utilised by other workers[23-25]. Sachadeva et al[26] utilised thermodynamic relation to evaluate the internal pressure in paraffins. Pandey et al[27] evaluated internal pressure in molten salts utilizing Flory Statistical Theory[16] to compute ultrasonic

velocity and Auerbach relation[15] to compute surface tension. An empirical relation based upon the empirical equations for thermal expansivity (α) and isothermal compressibility (β_T), was proposed and tested by Singh[10]. Suryanarayana[7,8] utilised free volume concept in conjunction with viscosity to formulate an empirical relation for the estimation of internal pressure of liquids. The relation has been utilised to evaluate internal pressure in liquids, by several workers[8,28-31]. From literature survey, it has been found that, detailed studies on analysis of all these relations to study their relative merits are still in dire need. The attempts to co-relate the internal pressure with other parameters are also scarce. This is an important part of study, as these relations have been purposed and derived in different approaches.

In the present work, various relations for estimation of internal pressure of liquids and liquid mixtures have been analyzed. Internal pressure and excess internal pressure of some binary and ternary liquid mixtures have also been calculated. An approach for estimating the internal pressure of liquids and liquid mixtures based upon the Flory statistical theory[16] has been also attempted. In this approach, the necessary parameters, thermal expansivity (α) and isothermal compressibility (β_T) have been evaluated using the relations based on the Flory statistical theory and these parameters have been then utilised to evaluate internal pressure. Though Flory statistical theory has been utilised by previous workers also, the present approach does not apply any empirical relation, unlike the previous studies. To the best of our knowledge, same approach of using the Flory statistical theory completely, i.e. without the use of any empirical relation, has not been attempted previously. The present approach is likely to give good results. The values of internal pressure of the liquids and liquid mixtures, as obtained using the various relations, have been utilised to study the relative merits of the relations and the nature of the molecular interactions. The thermodynamic relation for the evaluation of the internal pressure has been considered as an experimental method.

6.2 Theoretical

A number of relations can be utilised to estimate the internal pressure in pure liquids and liquid mixtures. Some of the important relations are summarized here.

a) ***Thermodynamic relation***

The relationship among applied pressure (p), molar volume (V), temperature (T) and molar internal energy (U), is given by thermodynamic relation:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad ...(i)$$

The isothermal internal energy-volume coefficient, $(\partial U/\partial V)_T$, is often called internal pressure (P_i). This equation can be used as a basis of experimental determination of internal pressure, with the help of isochors p vs T. So eq (i) can be written as:

$$P_i = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad ...(ii)$$

At limiting zero pressure or since external pressure usually is negligible as compared to the internal pressure, eq (ii) can be written as:

$$P_i = T\left(\frac{\partial p}{\partial T}\right)_V \qquad ...(1)$$

Since $\alpha = 1/V\ (\partial V/\partial T)_p$ and $\beta = -1/V\ (\partial V/\partial p)_T$, eq (ii) can be written as:

$$P_i = \frac{\alpha T}{\beta_T} - p \qquad ..(iii)$$

and for the pressure limiting to zero, eq (iii) can be written as:

$$P_i = \frac{\alpha T}{\beta_T} \qquad ...(2)$$

b) ***Relation derived from free volume***

Several workers[11-13] have made studies on free volume in liquids, which obviously is related to viscosity and internal pressure. From the work of Eyring, Hirschfelder and Kincad[11-13],

$$V_f = \left[\frac{bRT}{p + \left(\frac{\partial U}{\partial V}\right)_T}\right]^3 \frac{1}{V^2} \qquad ...(iv)$$

where, b is packing factor in liquid and is taken as 1.78 for closely packed hexagonal structure. Neglecting value of p, the eq (iv) can be written as:

$$V_f = \left[\frac{bRT}{P_i}\right]^3 \frac{1}{V^2} \qquad ...(v)$$

Suryanarayana and Kuppusami[7,8] proposed the following relation for free volume:

$$V_f = \left[\frac{Mu}{k\eta}\right]^{3/2} \qquad ...(vi)$$

where, η is the viscosity and k is dimensionless constant with a value of $4.28X10^9$.

From eqs (v) and (vi),

$$P_i = bRT\left(\frac{k\eta}{u}\right)^{1/2} \frac{\rho^{2/3}}{M^{7/6}} \qquad ...(3)$$

where, b=2, $k=4.28 \times 10^9$, η is in poise, u is in cm s^{-1} and ρ is in g cm^{-3}.

c) ***Relation using empirical equations for α and β_T***

The empirical relations for thermal expansion coefficient (α) and isothermal compressibility (β_T) are given as[10]:

$$\alpha = \frac{75.6 X 10^{-3}}{T^{1/9}\, u^{1/2}\, \rho^{1/3}} \qquad ...(vii)$$

and

$$\beta_T = \frac{17.1 X 10^{-4}}{T^{4/9}\, u^{2}\, \rho^{4/3}} \qquad ...(viii)$$

where, u is sound velocity in m s^{-1} and ρ is density in gm cm^{-3}. These relations for the estimation of α and β_T have been utilized to estimate internal pressure[10].

From eqs (2), (vii) and (viii) one gets

$$P_i = 44.2\ T^{4/3}\, u^{3/2}\, \rho \qquad ...(4)$$

where, u is in m s^{-1} and ρ is in g cm^{-3}.

d) ***Relation based upon Buehler-Hirschfelder-Curtiss equation of state***

According to the relation proposed by Buehler et al[5,6],

$$P_i V\left(1 - \frac{d}{a}\right) = RT \qquad ...(ix)$$

where, P_i is internal pressure, V is molar volume, 'd' is molecular diameter and 'a' is shortest distance between the nearest neighbour. The volume per molecule (V) is related to 'a' with the relation:

$$a = \frac{2^{1/6} V^{1/3}}{N^{1/3}} \qquad ...(x)$$

Using some suitable adjustment and eqs (ix) and (x), the internal pressure can be given as:

$$P_i = \frac{2^{1/6}\, RT}{2^{1/6}\, V - d\, N^{1/3}\, V^{2/3}} \qquad ...(5)$$

Molecular diameter required for eq (5) can be computed using the relation[14]:

$$d = \left(\frac{V\sigma^{1/4}}{7.2X10^{19}\, T_c^{1/4}} \right)^{2/5} \qquad ...(xi)$$

where, σ is surface tension and T_c is critical temperature. The surface tension (σ) can be calculated using the following relation[15]:

$$\sigma = 6.3 \text{X} 10^{-4}\, \rho\, u^{3/2} \qquad ...(xii)$$

where, ρ is in g cm^{-3} and u is in ms^{-1}.

Following relation can be used to calculate the critical temperature of liquid mixture:

$$T_c = \sum_{i=1}^{n} x_i (T_c)_i \qquad ...(xiii)$$

where, x_i and $(T_c)_i$ are mole fraction and critical temperature of components of the mixture.

e) ***Relation based upon Flory Statistical Theory***

Flory Statistical method is one of the most important methods for the evaluation of the various parameters of the liquid state. If the thermal expansivity (α) and isothermal expansivity (β_T) of pure liquid components are known, the values of α and β_T for liquid mixture of a given composition can be evaluated as using the relation:

$$(\alpha)_{Flory} = \frac{3\left(\tilde{V}^{1/3} - 1\right)}{\left[1 - 3(\tilde{V}^{1/3} - 1)\right] T} \qquad ...(xiv)$$

and

$$(\beta_T)_{Flory} = \frac{(\alpha)_{Flory}\, T\, \tilde{V}^2}{P^*} \qquad ...(xv)$$

Using the values of α and β_T thus obtained, one can evaluate the internal pressure of liquid mixture using the relation

$$P_i = \frac{(\alpha)_{Flory}\, T}{(\beta_T)_{Flory}} \qquad ...(6)$$

In the above equations, P* if characteristic pressure of the liquid mixture and is given by

$$P^* = T^* \sum \frac{\psi_i P_i^*}{T_i^*} \qquad ...(7)$$

where, ψ_i, P_i^* and T_i^* are the site fraction, characteristics pressure and characteristic temperature of the components of liquid mixtures. The details about the evaluation of these parameters, has been given in chapter-3 of this thesis. The present approach is supposed to provide a noble approach for the evaluation of the internal pressure in the liquid mixtures, as it uses the minimum input data like α, β_T and molar volume only of ***pure components***.

Some important properties of the liquids and liquid mixtures, which are, directly or indirectly, related to the internal pressure are discussed here.

a) Excess internal pressure (P_i^E)

The following relation can be utilised to compute the excess internal pressure of the liquid mixtures:

$$(P_i)^E = (P_i)_m - \sum_{i=1}^{n} x_i (P_i)_i \qquad ...(8)$$

where, x_i and $(P_i)_i$ are the mole fraction and internal pressure of the i^{th} component of the mixture.

b) Gruneisen Parameter (Γ) and excess Gruneisen parameter (Γ^E)

Gruneisen parameter (Γ) can be evaluated from the knowledge of specific heat ratio (γ) and thermal expansivity (α) as:

$$\Gamma = \frac{\gamma - 1}{\alpha T} \qquad ...(9)$$

The excess Gruneisen parameter (Γ^E) can be evaluated using the following relation:

$$\Gamma^E = \Gamma_m - \sum x_i \Gamma_i \qquad ...(10)$$

where, Γ_m is the Gruneisen parameter of liquid mixture and Γ_i is the Gruneisen parameter of i^{th} component of the liquid mixture. Sharma[9] has discussed the relationship between Gruneisen Parameter and the internal pressure.

c) Excess Enthalpy (H^E)

Relation between the excess enthalpy and excess enthalpy and excess internal pressure has been discussed by Rajendran[35], which can be given as:

$$H^E = \sum \left\{ x_i (Pi)_i V_i \right\} - (P_i)_m V \qquad ...(11)$$

However, the excess enthalpy can be evaluated more precisely using Flory theory also, the relation given as:

For binary liquid mixture:

$$H^E = \sum \left\{ x_i P_i^* V_i^* \left(\frac{1}{\tilde{V}_i} - \frac{1}{\tilde{V}} \right) \right\} + \frac{x_1 V_1^* \theta_2 X_{12}}{\tilde{V}} \qquad ...(12)$$

For ternary liquid mixture:

$$H^E = \sum\left\{x_i P_i^* V_i^*\left(\frac{1}{\widetilde{V}_i} - \frac{1}{\widetilde{V}}\right)\right\} + \frac{x_1 V_1^* \theta_2 X_{12}}{\widetilde{V}} + \frac{x_2 V_2^* \theta_3 X_{23}}{\widetilde{V}} + \frac{x_3 V_3^* \theta_1 X_{31}}{\widetilde{V}} \quad \ldots(13)$$

All the symbols used here have their usual meanings. These parameters have been discussed in chapter-3 of this thesis also.

6.3 Results and Discussion

Various pure liquids, some binary liquid mixtures and some ternary liquid mixtures of organic compounds, at varying temperatures have been taken under investigation for the present study. Internal pressure in liquids and liquid mixtures were computed using eqs (2) – (6). In binary and ternary liquid mixtures, excess internal pressure was computed using eq (8). In some binary liquid mixtures, excess Gruneisen parameter has also been evaluated using eq (10). The necessary data for the computation of these properties are taken from various sources[32-36].

The computed values of internal pressure and related parameters of pure liquids have been depicted in tables-1 to 6. Depending upon the availability of experimental data, different methods for the computation have been utilised. Some important results have been graphically represented in figures- 1 to 3. A closer perusal of table-1 and fig.1 reflects that there is obvious increase in internal pressure of higher homologues, in homologous series of alkanes. In fig. 1, the deviation pattern of internal pressure due to thermodynamic relation is more important, though the results from other methods have also been displayed for comparison purpose. In each alkane, internal pressure is found to decrease almost linearly, with increasing temperature. The possible reason for this behaviour of the liquids may be the decrease in cohesion with an increase in temperature owing higher perturbations. Tables-2, 3 and 5 show that compounds like cyclohexanol, methyl iodide, dioxane and chlorobenzene are found

to have relatively high internal pressure at a given set of physical conditions. These values reflect the nature of intermolecular force and size factors in the molecules.

As far as various methods for estimating internal pressure in pure liquids are concerned, eq (5) is found to give large deviations from the experimental results. The possible reason for the type of deviation this method yields could be that the relation is derived based upon some adjustments and the approach uses more than one empirical relations. This shows that eq (5) in the present form and approach cannot be recommended for most of the cases under investigation. Equation (4) is found to give satisfactory results in some cases (e.g. tables 1,2 and 5), where as in certain cases, the deviations are very high (e.g. table 6 and figures 2 & 3). Though eq (4) is a convenient method for the estimation of internal pressure with the help of minimum input data, the deviation as mentioned above show that there is a need of some adjustments in the eq (4). The differences in the calculated and experimental values of α and β_T (column 4 and 6 of table 2 and 3) also vouch for the same need. Equation (3), which is related with the free volume model, is found to give satisfactory results in some cases while there are larger deviations there also. These deviations show the need of re-evaluating the value of especially the factor 'b' used in this equation, which is usually taken as '2'. This method can be considered as an alternative and convenient method, when only viscometric, volumetric and ultrasonic data are available.

The computed values of internal pressure, excess internal pressure and other related parameters in some binary and ternary liquid mixtures have been depicted in tables -7 to 8. Due to similar computation involved, three different types of binary liquid mixtures have been listed together in table-7, as table 7(a), 7(b) and 7(c). Table - 8 shows the excess internal pressure as computed using eq (4). Even though the equation is empirical in nature, the pattern of the excess internal pressure obtained here is as expected for this system. Here, excess internal pressure is negative in whole concentration range of cyclohexane. Internal pressure of ternary liquid mixture

have been computed and depicted in table 9, 10 and 11 using the eq (3). The regular increase in excess internal pressure by the addition of chlorobenzene in chloroform + cyclohexane is observed. Tables 7(a), 7(b) and 7(c) enlist the experimental values of α, β_T, P_i and Pi^E. Some parameters, which were computed as a part of computation of these results, like surface tension (σ) and molecular diameter (d), have also been listed in tables 7(a), 7(b) and 7(c). Excess internal pressure (P_i^E) values listed here are computed using the thermodynamic relation only. There is almost systematic and expected change in P_i^E and Γ^E in most of the cases, showing that these excess properties may be utilised to study molecular interactions in liquid mixtures. In these systems, eq (4) is found to be partly applicable in some cases, whereas eq (5) in the present form is not applicable. There is an interesting and obvious increase in the internal pressure with changing the homologue in homologous series of alkanes, in the binary liquid mixtures of aromatic compounds + alkanes (table-7.c), which again may be due to the increased intermolecular forces of attractions in higher alkanes.

As expected while aiming the present study, Flory theory is found to give excellent results. The values of α and β_T as computed using Flory Statistical Theory [column 9^{th} and 10^{th} of tables 7(a) to 7(c)], also show good agreement with the experimental values. The present study can also be considered as an authentication for the method of computing internal pressure using Flory Statistical Theory related approach completely i.e. without the use of any empirical relation.

6.4 References

1. Richards T W, *Chem Rev*, **2** (1925) 315.
2. Dack M R, *J Chem Soc Rev (GB)*, **4** (1975) 211.
3. Hildebrand J H & Scott R L, "*Solubility of non-electrolyte*", 3rd ed, Reinhold, New York, 1950.
4. Hildebrand J H & Scott R L, "*Regular Solution*", Printice Hall, Englewood, Cliffs, 1962.

5. Buehler R J, Wentorff R H, Hirschfelder J O & Curtiss C F, *J Chem Phys*, **19** (1951) 61.
6. Hirschfelder J O, Curtiss C F & Bird R B, Molecular Theory of Liquids, John Wiley & Sons, ING New York, 1954
7. Suryanarayana C V & Kuppusami J, *J Acoust Soc Ind*, **4** (1976) 75.
8. Suryanarayana C V, *Ind J Pure & Appl Phys*, **27** (1989) 751.
9. Sharma B K, *Acustica*, **45** (1980) 65.
10. Singh A K, D Phil Thesis, University of Allahabad, 1995.
11. Eyring H & Hirschfelder J O, *J Phys Chem*, **41** (1937) 249.
12. Kincaid J F & Eyring H, *J Phys Chem*, **5** (1937) 587.
13. Kincaid J F & Eyring H, *J Phys Chem*, **6** (1938) 620.
14. Chaturvedi C V & Pratap S, *Acustica*, **42** (1979) 260.
15. Auerbach N, Experientia, **4** (1948) 473.
16. Flory P J, *J Am Chem Soc*, **87** (1965) 1833.
17. Barton A F M, *J Chem Edu*, **48** (1971) 156.
18. Barton A F M, *Chem Rev*, **75** (1975) 731.
19. Renuncio J A R, Breedveld G J F & Prausnitz J M, *J Phys Chem*, **81(4)** (1977) 324.
20. Pandey J D & Mishra R L, *Acustica*, **39** (1978) 200.
21. Pandey J D, J Chem Soc Farad Trans, **76** (1980) 1215.
22. Pandey J D, Pant N & Chaturvedi B R, *Chemica Scripta*, **18** (1981) 224.
23. Srivastava A P & Tripathi S N. *Current Science*, **55(4)** (1986) 180.
24. Acevedo I, Pedrosa G C & Katz M, *J Soln Chem*, **19(9)** (1990) 911.
25. Aminabhavi T M, Banerjee K & Balundgi R H, *Ind J Chem*, **38A** (1999) 768.
26. Sachdeva V K & Nanda V S, *J Chem Phys*, **75(9)** (1981) 4745.
27. Pandey J D, Gupta U & Singh A K, *Acoustics Letters*, **8(10)** (1985) 160.
28. Dhanalakshmi A, Lalitha V & Ganthimathi K, *J Acoust Soc Ind*, **XX(1-4)** (1992) 129.
29. Dhanalakshmi A, Lalitha V & Ganthimathi K, *J Acoust Soc Ind*, **XX(1-4)** (1992) 72.

30. Pandey J D, Hassan N A, Shukla J N & Dey R, *Acoustics Letters*, **23(6)** (1999) 123.
31. Arul G & Palaniappan L, *Ind J Pure & Appl Phys*, **39** (2001) 561.
32. Rajgopal E & Subramanyam S V, *J Chem Thermodyn*, **12** (1980) 797.
33. Low D I R & Hughes E A M, *Proc Roy Soc A*, **267** (1982) 384.
34. Aminabhavi T M, Aralaguppi M I, Gopalkrishna B & Khinnavar R S, *J Chem Eng Data*, **39** (1994) 522.
35. Rajendran V, *Ind J Pure & Appl Phys*, **32** (1994) 19.
36. Tardajos G, Aicart E, Costas M & Patterson D, *J Chem Soc Farad Trans*, **82** (1986) 2977.

Table - 1

Internal pressure of pure liquids various alkanes

T	ρ	u	α	β_T	P_i (10^5 N m^{-2})		
K	kg m^{-3}	m s^{-1}	10^{-3} K^{-1}	10^{-11} N^{-1} m^2	Expt.	Eqn 4	Eqn 5
n-pentane							
283.15	635.9	1077	1.431	180.8	2375	1847	1208
288.15	631.2	1053	1.447	190.6	2341	1815	1200
293.15	626.2	1030	1.465	201.0	2303	1781	1190
303.15	616.1	983	1.502	223.0	2220	1708	1170
n-hexane							
293.15	660.9	1098	1.393	162.7	2475	2071	1263
313.15	643.0	1008	1.457	197.3	2308	1934	1232
333.15	626.5	917	1.530	240.9	2111	1777	1198
n-heptane							
293.15	683.2	1152	1.345	140.4	2610	2299	1074
313.15	666.3	1067	1.399	166.8	2457	2183	1049
333.15	648.9	982	1.461	200.7	2288	2039	1019
353.15	631.1	898	1.533	245.0	2100	1872	984
n-decane							
293.15	729.7	1249	1.264	107.1	2809	2774	934
313.15	714.7	1175	1.302	123.4	2712	2707	919
333.15	699.4	1101	1.346	143.2	2592	2609	900
353.15	683.4	1027	1.395	167.2	2454	2482	877
363.15	675.6	990	1.422	181.2	2378	2410	865

Table-2

Internal pressure of cyclohexane and cyclohexanol

T	ρ	u	α	β_T	$\alpha_{eq\ (vii)}$	P_i (10^5 N m^{-2})		
K	kg m^{-3}	m s^{-1}	10^{-3} K^{-1}	10^{-11} N^{-1} m^2	10^{-3} K^{-1}	Expt.	Eqn 4	Eqn 5
Cyclohexanol								
298.15	945.1	1465.6	0.804	59.1	1.068	4058	4668	1794
313.15	933.6	1410.7	0.823	64.6	1.088	3993	4650	1788
323.15	926.0	1374.1	0.836	68.6	1.101	3938	4623	1783
Cyclohexane								
298.15	773.8	1249.5	1.215	112.8	1.237	3212	3009	1491
313.15	759.6	1177.5	1.265	129.0	1.275	3072	2885	1461
323.15	750.2	1129.2	1.294	141.1	1.303	2963	2790	1439

Table 3

Internal pressure of acetone and methyl iodide

T	ρ	u	α	β_T	$\alpha_{eq\ (vii)}$	P_i (10^5 N m^{-2})		
K	kg m^{-3}	M s^{-1}	10^{-3} K^{-1}	10^{-11} N^{-1} m^2	10^{-3} K^{-1}	Expt.	Eqn 4	Eqn 5
Acetone								
253.20	834.4	1365	1.332	90.4	1.175	3731	2979	1975
263.20	823.5	1321	1.344	97.1	1.195	3643	2948	1968
273.20	812.5	1275	1.361	105.5	1.216	3524	2898	1955
283.20	801.4	1230	1.380	114.3	1.239	3420	2842	1941
293.20	790.4	1185	1.398	123.9	1.264	3309	2776	1924
303.20	779.3	1140	1.416	134.5	1.290	3192	2701	1904
308.20	773.7	1117	1.435	141.1	1.303	3134	2658	1893
Methyl iodide								
253.20	2389.6	944	1.167	72.1	0.995	4101	4907	2892
263.20	2361.7	918	1.184	77.6	1.009	4017	4897	2877
273.20	2333.8	892	1.200	83.4	1.023	3931	4872	2858
283.20	2305.7	866	1.214	89.5	1.038	3841	4830	2836
293.20	2277.6	840	1.229	95.8	1.055	3760	4774	2811
303.20	2249.5	814	1.242	102.4	1.072	3676	4703	2783
308.20	2235.6	801	1.254	106.2	1.081	3640	4664	2768

Table – 4

Internal pressure of pure liquids: Diglyme and hexane

T	ρ	u	η	β_T	$\alpha_{eq\ (v.i)}$	P_i (10^5 N m^{-2})	
K	kg m^{-3}	m s^{-1}	10^{-1} Pa-s	10^{-11} N^{-1} m^2	10^{-3} K^{-1}	Eqn 3	Eqn 4
Diglyme							
298.15	939.9	1284	0.0099	89.5	1.144	2848	3808
303.15	935.6	1266	0.0091	92.0	1.151	2792	3794
308.15	930.1	1250	0.0084	94.4	1.159	2731	3782
313.15	925.7	1229	0.0079	97.6	1.168	2696	3750
318.15	920.1	1203	0.0073	102.0	1.181	2648	3686
Hexane							
298.15	661.2	1074	0.0030	204.5	1.406	2265	2049
303.15	656.7	1051	0.0029	214.0	1.422	2266	2015
308.15	651.8	1025	0.0027	225.6	1.441	2255	1968
313.15	647.3	1001	0.0026	237.0	1.459	2256	1927
318.15	642.4	980	0.0025	248.0	1.475	2260	1892

Table – 5

Internal pressure of various pure liquids at 303.15 K

T	ρ	u	α	β_T	η	P_i (10^5 N m^{-2})			
K	kg m^{-3}	m s^{-1}	10^{-3} K^{-1}	10^{-11} N^{-1} m^2	10^{-1} Pa-s	Expt.	Eqn 3	Eqn 4	Eqn 5
Compds									
C_6H_6	867.7	1278	1.320	102.7	0.0058	3896	3960	3570	2985
C_6H_{12}	766.2	1230	1.239	119.9	0.0080	3133	4002	2976	2403
Dioxane	1018.5	1325	1.115	78.7	0.0107	4294	5100	4420	3455
$C_6H_5CH_3$	853.9	1285	1.065	96.0	0.0054	3363	3098	3542	2528
C_6H_5Cl	1095.7	1250	0.990	78.9	0.0072	3804	3406	4359	2806
$CHCl_3$	1466.5	967	1.300	108.6	0.0061	3629	4016	3967	3781

Table - 6

Comparision of Internal pressure obtained from eqs (4) & 5 with experimental results in acetone and methyl iodide

T	ρ	u	α	β_T	$\alpha_{eq\ (vii)}$	%age diff in Pi	
K	kg m^{-3}	m s^{-1}	10^{-3} K^{-1}	10^{-11} N^{-1} m^2	10^{-3} K^{-1}	Eqn 4	Eqn 5
Acetone							
253.20	834.4	1365	1.332	90.4	1 175	20.15	47.07
263.20	823.5	1321	1.344	97.1	1.195	19.08	45.98
273.20	812.5	1275	1.361	105.5	1.216	17.76	44.52
283.20	801.4	1230	1.380	114.3	1.239	16.89	43.24
293.20	790.4	1185	1.398	123.9	1.264	16.12	41.86
303.20	779.3	1140	1.416	134.5	1 290	15.39	40.33
308.20	773.7	1117	1.435	141.1	1.303	15.19	39.59
Methyl iodide							
253.20	2389.6	944	1.167	72.1	0 995	-20.00	29.48
263.20	2361.7	918	1.184	77.6	1.009	-21.90	28.38
273.20	2333.8	892	1.200	83.4	1 023	-23.93	27.28
283.20	2305.7	866	1.214	89.5	1.038	-25.75	26.16
293.20	2277.6	840	1.229	95.8	1.055	-26.96	25.24
303.20	2249.5	814	1.242	102.4	1.072	-27.95	24.30
308.20	2235.6	801	1.254	106.2	1.081	-28.14	23.94

Table –7

Internal Pressure (P_i), Excess internal pressure (P_i^E) and related parameters of some binary liquid mixtures

7. a) Binary Liquid Mixture: Cyclohexane (1) + cyclohexanol (2)

T	x_1	α	$\beta_T/10^{-11}$	Thermodyn. Rel.			Flory Theory					Eq 4		Eq 5			Γ^E
K		$10^{-3}K^{-1}$	$N^{-1}m^2$	$Pi/10^5$	$P_i^{id}/10^5$	$P^E/10^5$	$V^{\sim}$	α_{Flory}	$\beta_{T(Flory)}$	$Pi/10^5$	% Dev	$Pi/10^5$	% Dev	$\sigma/10^{-3}$	d	$Pi/10^5$	
				N m^{-2}	N m^{-2}	N m^{-2}		$10^{-3}K^{-1}$	$10^{-11}N^{-1}m^2$	N m^{-2}		N m^{-2}		N m^{-1}	10^{-10} m	Nm^{-2}	
298.15	0.0000	1.215	112.77	3212	3212	0.00	1.290	1.215	112.77	3212	0.00	3009	6.33	21.5	5.38	1492	0.000
298.15	0.1977	1.128	102.90	3268	3380	-111.18	1.270	1.110	97.82	3383	-3.51	3171	2.99	22.7	5.38	1511	-0.062
298.15	0.3178	1.077	93.10	3449	3481	-32.05	1.259	1.054	90.08	3489	-1.15	3338	3.23	23.9	5.39	1541	-0.042
298.15	0.4185	1.047	88.00	3547	3566	-18.97	1.250	1.010	84.25	3574	-0.76	3522	0.73	25.2	5.40	1578	-0.041
298.15	0.5050	1.018	83.40	3639	3639	-0.15	1.242	0.974	79.66	3645	-0.17	3663	-0.64	26.2	5.41	1604	-0.044
298.15	0.6828	0.968	74.20	3890	3790	99.79	1.228	0.907	71.26	3795	2.44	4009	-3.06	28.7	5.43	1670	-0.004
298.15	0.7871	0.911	68.70	3954	3878	75.59	1.221	0.871	66.90	3882	1.82	4212	-6.52	30.1	5.44	1708	-0.008
298.15	0.9001	0.860	63.60	4032	3974	57.97	1.213	0.835	62.58	3978	1.32	4436	-10.04	31.7	5.46	1750	-0.001
298.15	1.0000	0.804	59.07	4058	4058	0.00	1.206	0.804	59.07	4058	0.00	4668	-15.04	33.4	5.47	1794	0.000
313.15	0.0000	1.265	128.97	3072	3072	0.00	1.311	1.265	128.97	3072	0.00	2885	6.08	19.3	5.36	1461	0.000
313.15	0.1977	1.145	115.80	3096	3254	-157.28	1.289	1.150	110.50	3259	-5.25	3036	1.95	20.3	5.35	1480	-0.076
313.15	0.3178	1.098	105.00	3275	3364	-89.59	1.276	1.088	101.10	3370	-2.91	3260	0.45	21.9	5.37	1525	-0.059
313.15	0.4185	1.064	98.40	3386	3457	-70.90	1.266	1.041	94.08	3465	-2.33	3426	-1.18	23.0	5.38	1556	-0.053
313.15	0.5050	1.034	92.20	3512	3537	-24.77	1.259	1.003	88.61	3545	-0.93	3570	-1.67	23.9	5.39	1583	-0.047
313.15	0.6828	0.973	81.60	3734	3700	33.57	1.243	0.931	78.69	3705	0.78	3936	-5.42	26.4	5.42	1654	-0.025
313.15	0.7871	0.927	75.80	3830	3797	33.18	1.235	0.893	73.60	3799	0.79	4152	-8.42	27.8	5.43	1694	-0.014
313.15	0.9001	0.875	70.00	3914	3901	13.79	1.226	0.855	68.59	3904	0.28	4391	-12.19	29.4	5.44	1739	-0.015
313.15	1.0000	0.823	64.55	3993	3993	0.00	1.219	0.823	64.55	3993	0.00	4650	-16.46	31.2	5.46	1788	0.000

7. b) Binary Liquid Mixture: Acetone + methyl iodide

T	x_1	α	$\beta_T/10^{-11}$	Thermodyn. Rel.			Flory Theory					Eq 4		Eq 5			
K		$10^{-3}K^{-1}$	$N^{-1}m^2$	$Pi/10^5$ N m^{-2}	$P_i^{id}/10^5$ N m^{-2}	$P^E/10^5$ N m^{-2}	V~	α_{Flory} $10^{-3}K^{-1}$	$\beta_{T(Flory)}$ $10^{-11}N^{-1}m^2$	$Pi/10^5$ N m^{-2}	% Dev	$Pi/10^5$ N m^{-2}	% Dev	$\sigma/10^{-3}$ N m^{-1}	d 10^{-10} m	$Pi/10^5$ Nm^{-2}	
253.20	0.0000	1.167	72.05	4101	4101	0.00	1.246	1.167	72.05	4101	0.00	4906	-19.62	43.7	4.55	2892	0.(
253.20	0.2000	1.269	78.86	4074	4027	47.41	1.252	1.201	75.64	4020	1.33	4409	-8.21	39.2	4.58	2643	-0.(
253.20	0.4000	1.298	83.20	3950	3953	-2.81	1.257	1.234	79.27	3942	0.22	3967	-0.43	35.3	4.60	2430	-0.(
253.20	0.6000	1.314	86.36	3853	3879	-26.37	1.263	1.267	82.94	3868	-0.40	3598	6.60	32.0	4.61	2257	-0.(
253.20	0.8000	1.324	88.72	3779	3805	-26.25	1.269	1.300	86.65	3799	-0.53	3273	13.37	29.1	4.63	2103	-0.(
253.20	1.0000	1.332	90.40	3731	3731	0.00	1.274	1.332	90.40	3731	0.00	2978	20.18	26.5	4.63	1974	0.(
263.20	0.0000	1.184	77.57	4017	4017	0.00	1.257	1.184	77.57	4017	0.00	4897	-21.90	41.4	4.55	2877	0.(
263.20	0.2000	1.277	84.58	3974	3942	31.38	1.263	1.216	81.39	3932	1.04	4386	-10.36	37.1	4.57	2628	-0.(
263.20	0.4000	1.310	89.51	3852	3868	-15.51	1.268	1.249	85.25	3856	-0.11	3929	-2.00	33.2	4.59	2414	-0.(
263.20	0.6000	1.326	93.07	3750	3793	-42.66	1.274	1.281	89.16	3782	-0.84	3561	5.03	30.1	4.61	2243	-0.(
263.20	0.8000	1.335	95.53	3678	3718	-39.49	1.279	1.312	93.11	3709	-0.83	3239	11.94	27.4	4.62	2093	-0.(
263.20	1.0000	1.344	97.11	3643	3643	0.00	1.285	1.344	97.11	3643	0.00	2948	19.08	24.9	4.63	1968	0.0(
273.20	0.0000	1.200	83.40	3931	3931	0.00	1.268	1.200	83.40	3931	0.00	4872	-23.93	39.2	4.54	2858	0.00
273.20	0.2000	1.282	90.70	3862	3850	11.92	1.274	1.232	87.67	3839	0.58	4345	-12.53	34.9	4.57	2608	-0.04
273.20	0.4000	1.316	95.93	3748	3768	-20.48	1.279	1.265	92.02	3756	-0.21	3881	-3.56	31.2	4.59	2395	-0.10
273.20	0.6000	1.333	99.98	3642	3687	-44.54	1.285	1.297	96.44	3674	-0.87	3513	3.55	28.2	4.60	2226	-0.10
273.20	0.8000	1.347	103.13	3568	3606	-37.40	1.291	1.329	100.94	3597	-0.80	3189	10.62	25.6	4.62	2079	-0.06
273.20	1.0000	1.361	105.50	3524	3524	0.00	1.296	1.361	105.50	3524	0.00	2898	17.76	23.3	4.62	1955	0.00(
283.20	0.0000	1.214	89.51	3841	3841	0.00	1.278	1.214	89.51	3841	0.00	4830	-25.75	37.0	4.54	2836	0.00(

283.20	0.2000	1.292	97.01	3772	3757	15.04	1.284	1.247	94.27	3746	0.68	4292	-13.79	32.9	4.56	2586
283.20	0.4000	1.323	103.13	3633	3672	-39.36	1.290	1.280	99.13	3657	-0.65	3828	-5.35	29.3	4.58	2376
283.20	0.6000	1.342	107.87	3523	3588	-64.83	1.296	1.314	104.08	3575	-1.48	3453	1.99	26.5	4.60	2207
283.20	0.8000	1.361	111.52	3456	3504	-47.60	1.302	1.347	109.14	3495	-1.13	3132	9.39	24.0	4.61	2063
283.20	1.0000	1.380	114.29	3420	3420	0.00	1.308	1.380	114.29	3420	0.00	2842	16.89	21.8	4.61	1941
293.20	0.0000	1.229	95.83	3760	3760	0.00	1.289	1.229	95.83	3760	0.00	4774	-26.96	34.9	4.54	2811
293.20	0.2000	1.300	103.92	3668	3670	-2.23	1.295	1.263	101.16	3661	0.20	4223	-15.13	30.9	4.56	2560
293.20	0.4000	1.332	110.93	3521	3580	-59.25	1.301	1.296	106.63	3564	-1.22	3755	-6.67	27.5	4.57	2352
293.20	0.6000	1.355	116.46	3411	3490	-78.34	1.308	1.330	112.23	3475	-1.85	3377	1.01	24.7	4.59	2184
293.20	0.8000	1.377	120.90	3339	3400	-60.09	1.314	1.364	117.98	3390	-1.51	3056	8.49	22.4	4.60	2042
293.20	1.0000	1.398	123.86	3309	3309	0.00	1.320	1.398	123.86	3309	0.00	2776	16.12	20.3	4.61	1924
303.50	0.0000	1.242	102.44	3680	3680	0.00	1.299	1.242	102.44	3680	0.00	4710	-27.99	32.9	4.53	2786
303.50	0.2000	1.306	111.52	3554	3583	-28.44	1.306	1.276	108.47	3570	-0.45	4145	-16.63	29.0	4.55	2533
303.50	0.4000	1.339	119.81	3392	3486	-93.78	1.312	1.311	114.69	3469	-2.28	3668	-8.15	25.6	4.57	2325
303.50	0.6000	1.364	126.03	3285	3389	-103.99	1.319	1.346	121.11	3373	-2.69	3295	-0.30	23.0	4.58	2161
303.50	0.8000	1.390	130.87	3224	3292	-68.18	1.325	1.381	127.72	3282	-1.80	2983	7.46	20.8	4.60	2023
303.50	1.0000	1.416	134.52	3195	3195	0.00	1.332	1.416	134.52	3195	0.00	2704	15.36	18.9	4.60	1906

7. c) Binary Liquid Mixture: Equimolar mixtures of aromatic compounds+ alkanes at 298.15K

Liquid Mixtures	α	$\beta_T/10^{-11}$	Thermodyn. Rel.			Flory Theory					Eq 4		Eq 5			
	$10^{-3}K^{-1}$	$N^{-1}m^2$	$Pi/10^5$	$P_i^{id}/10^5$	$P^E/10^5$	$V^{\sim}$	α_{Flory}	$\beta_{T(Flory)}$	$Pi/10^5$	% Dev	$Pi/10^5$	% Dev	$\sigma/10^{-3}$	d	$Pi/10^5$	
			N m^{-2}	N m^{-2}	N m^{-2}		$10^{-3}K^{-1}$	$10^{-11}N^{-1}m^2$	N m^{-2}		N m^{-2}		N m^{-1}	10^{-10} m	Nm^{-2}	
Benzene+C6	1.305	135.35	2875	3113	-238.49	1.307	1.306	129.64	3004	-4.48	2564	10.82	18.3	5.35	1377	-0.07
Benzene+C8	1.178	118.71	2959	3229	-269.88	1.287	1.199	114.16	3131	-5.84	2775	6.22	19.9	5.66	1277	-0.1(
Benzene+C10	1.099	108.52	3019	3298	-278.76	1.275	1.135	105.38	3211	-6.35	2940	2.64	21.0	5.95	1195	-0.11
Benzene+C12	1.041	101.09	3070	3355	-285.03	1.267	1.097	99.80	3277	-6.74	3072	-0.05	22.0	6.22	1128	-0.13
Benzene+C14	0.991	95.43	3096	3405	-308.63	1.261	1.068	95.41	3337	-7.79	3183	-2.80	22.8	6.48	1072	-0.15
Benzene+C16	0.960	91.28	3136	3449	-313.00	1.258	1.048	92 20	3389	-8.08	3280	-4.62	23.5	6.72	1026	-0.16
Tolune+C6	1.231	126.81	2894	3005	-110.52	1.292	1.227	124.79	2932	-1.29	2663	7.98	19.1	5.51	1321	-0.03
Toluene+C8	1.128	113.84	2954	3120	-165.91	1.273	1.126	109.86	3056	-3.44	2841	3.85	20.3	5.81	1226	-0.06
Toulene+C10	1.057	104.19	3025	3190	-165.10	1.261	1.065	101.35	3133	-3.58	3010	0.49	21.5	6.09	1155	-0.07
Toluene+C12	1.011	98.32	3066	3247	-181.14	1.254	1.030	96.01	3199	-4.33	3125	-1.94	22.4	6.35	1091	-0.09
Toluene+C14	0.972	93.02	3115	3296	-180.96	1.248	1.003	91.81	3257	-4.55	3241	-4.03	23.2	6.59	1042	-0.1(
Toluene+C16	0.943	89.16	3153	3340	-186.93	1.245	0.985	88.77	3308	-4.91	3336	-5.79	23.9	6.82	999	-0.1(
Chlr.benz.+C6	1.171	114.50	3049	3172	-123.27	1.280	1.162	112.58	3077	-0.92	2964	2.79	21.2	5.50	1394	-0.04
Chlr.benz.+C8	1.084	104.20	3102	3288	-186.17	1.262	1.071	99.82	3199	-3.14	3128	-0.86	22.4	5.80	1287	-0.0(
Chlr.benz.+C10	1.023	97.10	3141	3357	-216.32	1.251	1.016	92.46	3276	-4.30	3253	-3.57	23.3	6.07	1199	-0.08
Chlr.benz +C12	0.978	91.70	3180	3415	-234.79	1.244	0.984	87.81	3341	-5.07	3365	-5.83	24.1	6.33	1131	-0.1(
Chlr.benz.+C14	0.946	87.80	3212	3464	-251.70	1.239	0.959	84.14	3398	-5.78	3453	-7.50	24.7	6.58	1073	-0.1
Chlr.benz.+C16	0.921	84.40	3254	3508	-254.48	1.236	0.942	81.48	3447	-5.95	3541	-8.84	25.3	6.81	1027	-0.1

Table - 8

Internal pressure of binary liquid mixture: Cyclohexane (1) + benzene (2)

(calculated using equation 4)

T	x_1	x_2	ρ	u	α_{calc}	$\beta_{T\,calc}$	P_i $(10^5\ N\ m^{-2})$		
K			*kg m^{-3}*	*m s^{-1}*	*10^{-3} K^{-1}*	*10^{11} N^{-1} m^2*	$(P_i)_m$	$(P_i)_{id}$	$(P_i)^E$
303.15	0.198	0.802	842.0	1253	1.199	108.1	3362.3	3448.4	-86.1
	0.400	0.600	818.6	1238	1.217	114.9	3210.4	3330.4	-120.0
	0.501	0.500	808.6	1231	1.226	118.2	3144.3	3271.6	-127.3
	0.604	0.396	799.3	1228	1.232	120.6	3096.8	3211.2	-114.4
	0.800	0.200	783.1	1225	1.242	124.5	3022.9	3096.9	-74.0
323.15	0.198	0.802	821.4	1155	1.250	127.8	3161.0	3251.2	-90.2
	0.400	0.600	798.2	1142	1.269	135.8	3020.0	3135.5	-115.4
	0.501	0.500	788.4	1136	1.278	139.5	2959.5	3077.9	-118.4
	0.604	0.396	779.2	1133	1.284	142.5	2913.3	3018.5	-105.2
	0.800	0.200	763.5	1127	1.297	147.9	2832.0	2906.4	-74.4

Table – 9

Internal pressure of ternary liquid mixture:

Benzene (1) + chloroform (2) + cyclohexane (3) - calculated using equation 3

T	x_1	x_3	ρ	u	η	P_i $(10^5\ N\ m^{-2})$		
K			*kg m^{-3}*	*m s^{-1}*	*10^{-1} Pa-s*	$(P_i)_m$	$(P_i)_{id}$	$(P_i)^E$
303.15	0.1015	0.5966	945.3	1125	0.00629	3738.0	4002.0	-264.1
	0.2019	0.4991	957.4	1122	0.00602	3723.9	3997.7	-273.8
	0.2998	0.4009	965.6	1129	0.00582	3699.9	3993.5	-293.6
	0.4001	0.2997	981.3	1134	0.00572	3726.3	3989.2	-262.9
	0.5045	0.1972	996.3	1142	0.00564	3756.5	3984.7	-228.3
	0.6031	0.0993	1011.9	1146	0.00563	3816.3	3980.5	-164.2

Table 10

Internal pressure of ternary liquid mixture:

Toulene (1) + chloroform (2) + cyclohexane (3) - calculated using equation 3

T	x_1	x_3	ρ	u	η	P_i (10^5 N m^{-2})		
K			kg m^{-3}	m s^{-1}	10^{-1} Pa-s	$(P_i)_m$	$(P_i)_{idl}$	$(P_i)^E$
303.15	0.0911	0.5404	981.5	1106	0.00617	3658.1	3924.9	-266.8
	0.2198	0.4863	947.8	1134	0.00602	3556.8	3807.6	-250.8
	0.3004	0.3960	962.7	1143	0.00589	3499.6	3734.8	-235.3
	0.4013	0.2961	969.1	1145	0.00571	3425.0	3643.6	-218.7
	0.5016	0.1985	981.3	1152	0.00562	3388.2	3552.9	-164.7
	0.5976	0.0989	994.8	1159	0.00562	3372.7	3466.2	-93.5

Table 11

Internal pressure of ternary liquid mixture:

Chlorobenzene (1) + chloroform (2) + cyclohexane (3) – calculated using equation 3

T	x_1	x_3	ρ	u	η	P_i (10^5 N m^{-2})		
K			kg m^{-3}	m s^{-1}	10^{-1} Pa-s	$(P_i)_m$	$(P_i)_{idl}$	$(P_i)^E$
303.15	0.1001	0.5965	965.9	1126	0.00647	3682.7	3946.7	-264.0
	0.1988	0.4978	999.8	1132	0.00646	3632.8	3887.8	-255.0
	0.3150	0.3975	1032.6	1141	0.00645	3581.5	3818.2	-236.7
	0.4005	0.3001	1076.8	1142	0.00650	3580.6	3767.3	-186.7
	0.5023	0.1995	1111.6	1151	0.00663	3563.9	3706.6	-142.7
	0.5997	0.0996	1148.8	1156	0.00674	3557.1	3648.5	-91.4

Table 10

Internal pressure of ternary liquid mixture:

Toulene (1) + chloroform (2) + cyclohexane (3) - calculated using equation 3

T	x_1	x_3	ρ	u	η	P_i (10^5 N m^{-2})		
K			kg m^{-3}	m s^{-1}	10^{-1} Pa-s	$(P_i)_m$	$(P_i)_{idl}$	$(P_i)^E$
303.15	0.0911	0.5404	981.5	1106	0.00617	3658.1	3924.9	-266.8
	0.2198	0.4863	947.8	1134	0.00602	3556.8	3807.6	-250.8
	0.3004	0.3960	962.7	1143	0.00589	3499.6	3734.8	-235.3
	0.4013	0.2961	969.1	1145	0.00571	3425.0	3643.6	-218.7
	0.5016	0.1985	981.3	1152	0.00562	3388.2	3552.9	-164.7
	0.5976	0.0989	994.8	1159	0.00562	3372.7	3466.2	-93.5

Table 11

Internal pressure of ternary liquid mixture:

Chlorobenzene (1) + chloroform (2) + cyclohexane (3) – calculated using equation 3

T	x_1	x_3	ρ	u	η	P_i (10^5 N m^{-2})		
K			kg m^{-3}	m s^{-1}	10^{-1} Pa-s	$(P_i)_m$	$(P_i)_{idl}$	$(P_i)^E$
303.15	0.1001	0.5965	965.9	1126	0.00647	3682.7	3946.7	-264.0
	0.1988	0.4978	999.8	1132	0.00646	3632.8	3887.8	-255.0
	0.3150	0.3975	1032.6	1141	0.00645	3581.5	3818.2	-236.7
	0.4005	0.3001	1076.8	1142	0.00650	3580.6	3767.3	-186.7
	0.5023	0.1995	1111.6	1151	0.00663	3563.9	3706.6	-142.7
	0.5997	0.0996	1148.8	1156	0.00674	3557.1	3648.5	-91.4

Fig. 1: Internal pressure of alkanes at varying temperature using various relations

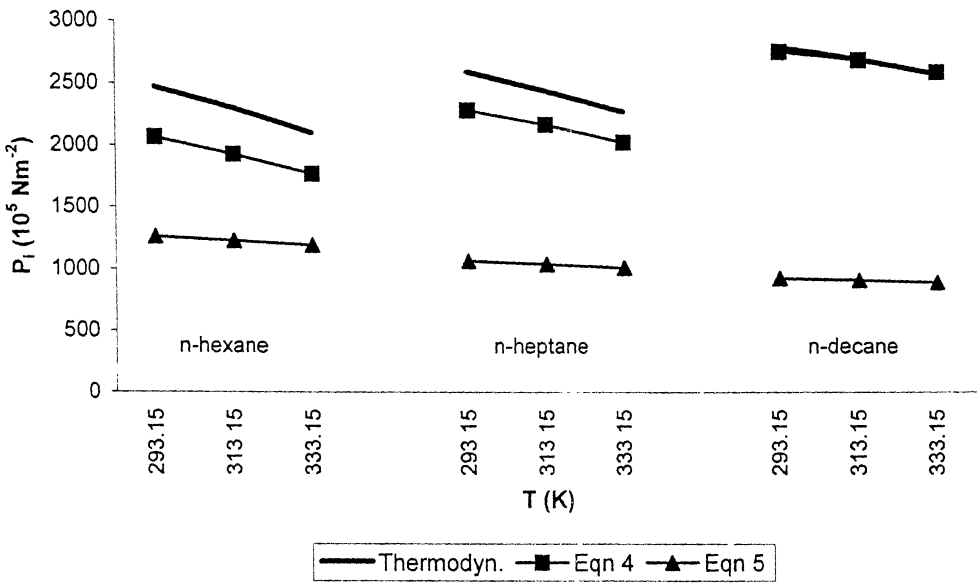


Fig. 2: Internal pressure of methyl iodide at varying temperature using various relations

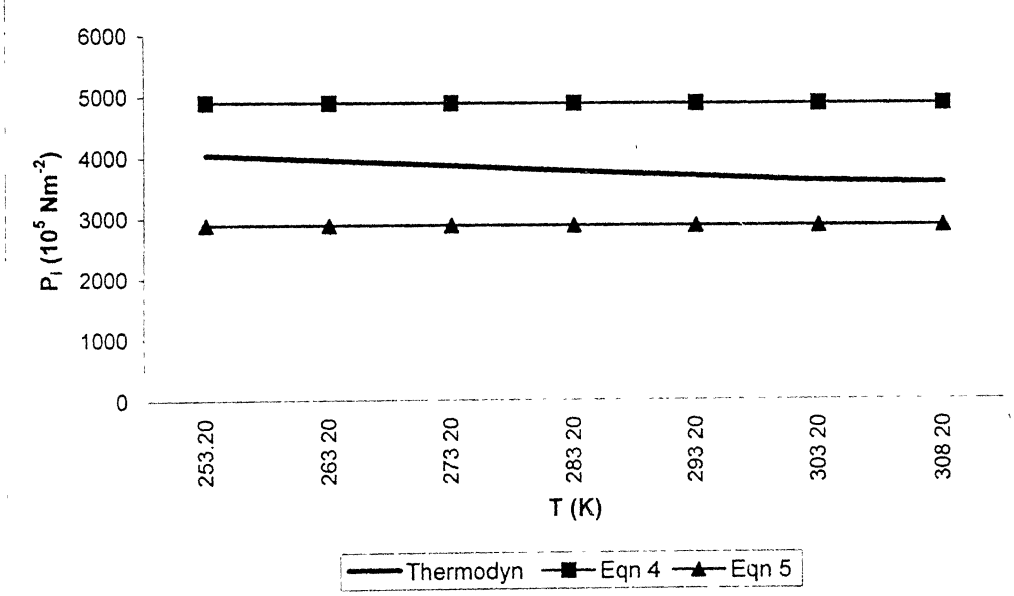


Fig. 3: Internal pressure of acetone at varying temperature using various relations

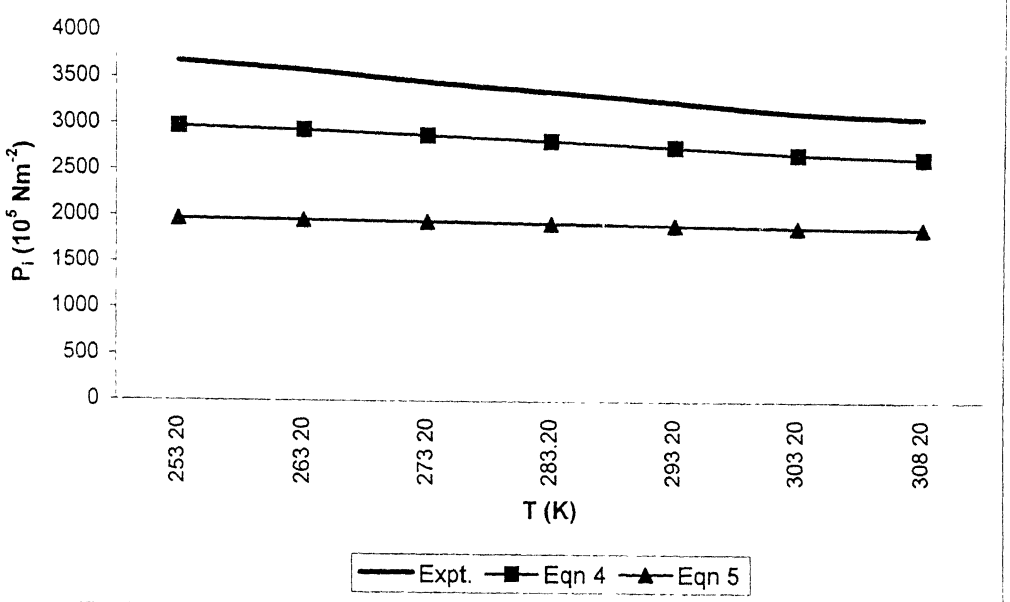
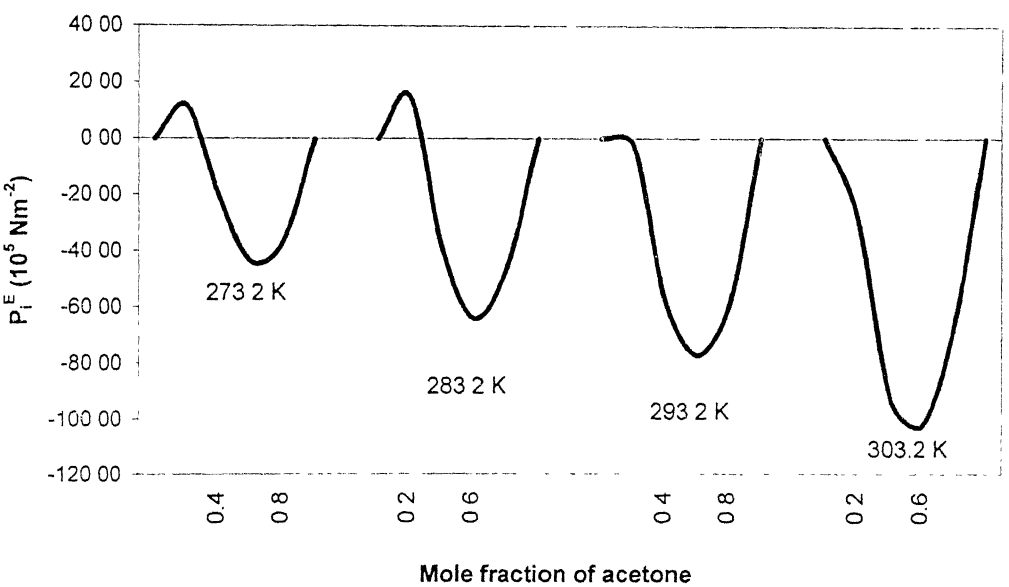


Fig. 4: Internal pressure of binary liquid mixture: Acetone (1) + methyl iodide (2)



CHAPTER – 7

Thermoacoustical, anharmonic, non-linear and related volumetric properties of liquids and liquid mixtures

7.1 Introduction

Thermoacoustical, anharmonic and non-linear Properties

Thermoacoustical and anharmonic properties of liquids and liquid mixtures have gained enormous amount of interest for a long time. The properties, which had been applied to study solid crystalline state, have now been applied for liquid state as liquids support a quasi-crystalline model for their structure.

Grüneisen parameter (Γ) is one of the important parameters which is used to study internal structure, clustering phenomenon and thermodynamic properties of solid crystalline lattice [1-3]. In the theory of lattice vibrations, if harmonic approximations are assumed, linear waves are supposed to follow principle of superposition i.e. waves do not interact with each other. In reality, the waves interact with each other causing anharmonicity. Due to such anharmonic bahaviour, properties like lattice thermal resistivity and thermal expansion arise. The extent of such anharmonity of lattice is characterised by Grüneisen parameter.

Knopoff and Shapiro[4] extended the use of this parameter for the liquids. To extend the use of this parameter for the structural study of liquids, Pseudo-Grüneisen parameter (Γ_G) is introduced. Pseudo-Grüneisen parameter (Γ_G) has been evaluated in liquids and liquid mixtures by several workers[5-7]. Pandey[8] evaluated some acoustical parameters like Rao constant (Y)[9], Wada constant (W)[10] and Γ_G in liquid fluorine at varying temperatures and pressures, employing ultrasonic and volumetric data. Compressional study of liquid fluorine was performed with the help of Pseudo-Grüneisen parameter and coefficient of thermal expansion (α). It was shown that $\Gamma\alpha$ decreases with increasing compression i.e. with increasing pressure on liquid fluorine.

Sharma[11-12] utilised ultrasonic and volumetric data to evaluate Pseudo-Grüneisen parameter, solubility parameter and internal pressure in various liquids. It was shown

that these three properties generally decrease linearly with increasing temperature for most of the liquids under investigation.

Various thermoacoustical and non-linear properties like Carnevale & Litovitz exponent (K')[13], molecular constant (n_M) and Beyer's non-linearity parameter (B/A)[14] were evaluated in some liquids by Sharma[15]. Dependence of B/A with K' was analysed. A number of thermoacoustical parameters and non-linearity parameter for liquid state were analysed. It was shown that non-linearity parameter depends upon both Rao's exponent and Carnevale & Litovitz exponent. Thermal expansion coefficient (α) was used as a key parameter to derive various relationships. Pseudo-Grüneisen parameter, non-linear and various thermoacoustical parameters were evaluated in various organic liquids and polymers by Sharma[16-19]. In all these studies, thermal expansion coefficient (α) was taken as major parameter for evaluating the various other properties of liquids. A new parameter, Sharma Parameter (S) was introduced[17], which again can be calculated by the knowledge of thermal expansion coefficient. Sharma[20] evaluated various thermoacoustical properties and Sharma parameter in various metals, metal halides, fluorocarbon fluids, liquid helium isotopes and many organic liquids.

Pandey et al[21] evaluated various thermoacoustical and non-linear parameters in various liquids under varying physical conditions. Sharma[22] evaluated various thermoacoustical, anharmonic and non-linear parameters and their inter-relationships. Pandey et al[23] studied temperature and pressure dependence of thermoacoustical parameters of liquid argon and xenon. Tabhane et al[24] evaluated some thermoacoustical properties in some liquid mixtures at 298K.

Literature survey shows that extensive study of thermoacoustical and anharmonic properties has been limited to the studies on liquids. Though some studies on thermoacoustical parameters of liquid mixtures have been attempted[24], the number of parameters evaluated are limited and have been evaluated for one temperature only.

In this chapter, an attempt has been made to evaluate various thermoacoustical and anharmonic properties of liquid and liquid mixtures at varying conditions and use them to co-relate with molecular interactions. Some properties, which are not studied previously for liquid mixtures using thermal expansivity data (like δ, Γ_G, B/A etc.), have also been evaluated. The greatest advantage of this approach is the computation of the parameters using the minimum input of data (mostly thermal expansivity).

Available volume from thermoacoustical parameters

The available volume is a very useful quantity, which reflects the extent of intermolecular interactions in liquids and liquid mixtures. The easy and accurate method for its determination provides useful means of studying intermolecular interactions and other thermodynamic properties.

By the use of thermoacoustical parameters, available volume can be estimated easily[20]. From the literature survey, it has been found that no attempt has been made to compute free volume in organic liquids and their mixture using thermoacoustical parameters. This chapter aims to compute available volume in pure liquids and liquid mixtures at varying temperatures using thermoacoustical parameters and correlate the values obtained with the values obtained from thermodynamic relation of available volume. The work will also provide a novel approach for correlating thermoacoustical parameters with available volume and many other related parameters.

7.2 Theoretical

Thermoacoustical, anharmonic and non-Linear Properties

Temperature and pressure dependence of thermal expansion coefficient (α) has been utilised[15,19] to get various relations to evaluate thermoacoustical parameters of liquids. Isobaric acoustical parameter (K) due to Rao[9], isothermal acoustical parameter (K') due to Carnevale and Litovitz[13] and isochoric acoustical parameter (K") due to Sharma[15,20] are as follows:

$$K = -\frac{1}{\alpha}\left(\frac{d\ln u}{dT}\right)_p = -\left(\frac{\mathrm{d}\ln \mathrm{u}}{\mathrm{d}\ln \mathrm{V}}\right)_P = \frac{1}{2}\left[1 + \frac{\mathrm{S}^*(1+\alpha\mathrm{T})}{\alpha\mathrm{T}}\right] = \mathrm{K'\text{-}K''} \qquad ...(1)$$

$$K' = \frac{1}{\beta}\left(\frac{d\ln u}{dP}\right)_T = -\left(\frac{\mathrm{d}\ln \mathrm{u}}{\mathrm{d}\ln \mathrm{V}}\right)_T = \frac{1}{2}\left[3 + \frac{\mathrm{S}^*(1+\alpha\mathrm{T}) + \mathrm{X}}{\alpha\mathrm{T}}\right] = \mathrm{K} + \mathrm{K''} \qquad ...(2)$$

$$K'' = \frac{1}{\alpha}\left(\frac{d\ln u}{dT}\right)_V = -\frac{1}{2\alpha\mathrm{T}}\left(\frac{\mathrm{d}\ln \beta}{\mathrm{d}\ln \mathrm{T}}\right)_V = 1 + \frac{\mathrm{X}}{2\alpha\mathrm{T}} = \mathrm{K'\text{-}K} \qquad ...(3)$$

where, u is ultrasonic velocity, β is isothermal compressibility and X is isochoric temperature coefficient of internal pressure, which is given by:

$$X = \left(\frac{d\ln P_i}{d\ln T}\right)_V = -\frac{2\mathrm{S}^*\mathrm{S}_o^*}{\tilde{V}^{C_1}} = -\frac{2(1+2\alpha\mathrm{T})}{\tilde{V}^{C_1}} \qquad ...(4)$$

where, S_o is Sharma parameter[17] and C_1 is Moelwyn-Hughes Parameter[25], which is the temperature and pressure coefficient of bulk modulus. Sharma parameters (S_o,S_o^* & S^*)[17,20] are given by:

$$S_o = -\frac{X}{2}(3+4\alpha T) = \frac{3\mathrm{S}^*(1+2\alpha\mathrm{T})}{\tilde{\mathrm{V}}^{C_1}} = (1+2\alpha\mathrm{T})\frac{3+4\alpha\mathrm{T}}{\tilde{\mathrm{V}}^{C_1}} \qquad ...(5)$$

$$S_o^* = \frac{1+2\alpha\mathrm{T}}{\mathrm{S}^*} = \frac{1+2\alpha\mathrm{T}}{1+4\alpha t/3} \qquad ...(6)$$

$$S^* = 1 + \frac{4\alpha\mathrm{T}}{3} \qquad ...(7)$$

Moelwyn-Hughes parameter (C_1), which is used to study surface properties, is given by:

$$C_1 = \left(\frac{d\ln\alpha}{d\ln T}\right)_V = \left(\frac{\mathrm{d}\ln\alpha}{\mathrm{d}\ln \mathrm{T}}\right)_P + \frac{\alpha\mathrm{T}}{\beta}\left(\frac{\mathrm{d}\ln\alpha}{\mathrm{dP}}\right)_T = \frac{13}{3} + \frac{1}{\alpha\mathrm{T}} + \frac{4\alpha\mathrm{T}}{3} \qquad ...(8)$$

Reduced volume ($\tilde{V}$) can be calculated using the relations:

$$\tilde{V} = \left(\frac{S^*}{1+\alpha T}\right)^3 = \left[1+\frac{\alpha T}{3(1+\alpha t)}\right]^3 \qquad ...(9)$$

Huggin's parameter (F) [26,27] in terms of temperature and pressure derivatives of compressibility and Sharma parameter[20] can be expressed as:

$$F = 1+\frac{2\alpha T}{3}+\left(\frac{d\ln\beta}{d\ln T}\right)_V = 2\left[1+\frac{S_0}{3S^*}\right] - S^* \qquad ...(10)$$

Molecular constant (n_M) can be evaluated in terms of X as:

$$n_M = \frac{1}{1+X/2} \qquad ...(11)$$

Fractional free volume (f), which is the measure of molecular disorder, can be evaluated from thermoacoustical parameters as:

$$f = \frac{1}{K'+1} \qquad ...(12)$$

Anharmonic and non-linear parameters like Grüneisen parameter (Γ_G), Anderson-Grüneisen parameter (δ), which is important property to study internal structure, and Beyers's non-linearity parameter (B/A) in terms of thermal expansivity are given by:

$$\Gamma_G = \frac{\gamma - 1}{\alpha T} \qquad ...(13)$$

$$\delta = \frac{7}{3}+\frac{1}{\alpha T} \qquad ...(14)$$

$$B/A = 2\gamma K''+2K \qquad ...(15)$$

Available volume from thermoacoustical parameters

The available volume can be deduced using thermoacoustical parameter K' as:

$$V_a = \frac{V}{K'+1} \qquad ...(16)$$

Using thermodynamic relation, available volume can be computed using the following relation:

$$V_a = V - \left[V \left(1 - \frac{T}{T_c} \right)^{0.3} \right] \qquad ...(17)$$

7.3 Results and Discussion

Thermoacoustical, anharmonic and non-Linear Properties

Thermoacoustical, anharmonic and non-linear properties of various liquids and liquid mixtures were calculated using various relations (eqs 1-15). The results thus obtained have been depicted in tables 1-2 and graphically represented in figures 1-2. The necessary data for the calculation have been taken from literature[28-33].

Table-1 represents the insight of the thermoacoustical, anharmonic and non-linear properties in pure liquids. The dependence of important properties, Γ_G and δ, of pure liquids with temperature has been represented in fig.1.

Thermal expansivity data is controlling factor for the evaluation of all these parameters, due to its dependence on temperature. From table-1, it is clear that, there is regular increase in Sharma parameter (S^*), reduced volume (V^-) and isochoric temperature coefficient of internal pressure (X_i) with a rise in temperature. The calculated values of S^* for the organic liquids under investigation are found to be in a range of 1.22 to 1.69, which can be compared with the values 1.0 to 1.5 for crystalline solid and melts[20], about 1.27 for polymers[17], 1.0 to 1.3 for many simple liquids[21] and about 1.2 to 1.6 for most of organic liquids[20]. The values of X are found

to be –ve for the organic liquids under investigation, as observed earlier for other systems[20]. It is interesting to note that, there is regular and sharp relationship between S^* and X. As X is related to internal pressure directly, the parameter S^* can be utilised to evaluate the internal pressure of liquids, which can turn to be a new approach. Though, the relation to compute internal pressure using thermoacoustical parameter has been given, the existing relation does not provide the satisfactory results. The values of Moelwyn-Hughes parameter (C_1) are found to decrease linearly with increasing temperature. These values can be compared with the values 7.0 to 15.0 for various polymers[19]. Huggin's parameter (F) is found to in a range of 0.74 to 1.39, which can be compared with the values, 1.5 to 1.7 for alkali halides and metals, 1.2 to 1.8 for poly-crystalline solids and about 1 for many spherical molecules[20]. Values of K, K', K", n_M and S_0 are found to be more or less similar to those obtained in variety of other compounds[20].

Fractional free volume (f), which is expressed in terms of repulsive exponent of intermolecular potential, is found to have the values in a range of 0.20 to 0.22. Values of f are low in almost all the polymers[22]. The possible reason for these low values of f in polymer is due to decrease in molecular disorderness. The greater value of f in ordinary organic liquids may be assumed to reflect greater disorderness of molecules and thus cause decrease in anharmonicity and low values of Pseudo-Grüneisen parameter. Psudo-Gruneisen parameter decreases with increasing temperature as evident from table-1 and fig.1.(c), due to the same reason as mentioned above. In most of the cases of pure liquids, non-linearity parameter (B/A) is found to increase with increasing temperature. The computed values of various thermoacoustical, anharmonic and non-linear properties of liquid mixtures have been shown in table-2. The obvious regular variation in the properties with increasing mole fraction of one of the components is observed in all the cases. The obvious regular change in non-linearity parameter (B/A) is also observed in binary liquid mixtures (table-2 and fig. 2.b). The regular and obvious change in various properties with increasing homologue is observed in case of equimolar mixtures of aromatic

compounds with alkanes (table-2.f). These results prove the applicability of the relations (1-15) for pure liquids as well as for liquid mixtures.

Available volume from thermoacoustical parameters

The values of some thermoacoustical parameters obtained from expansivity data and the values of available volume obtained from both the methods (eqs 16 and 17) are displayed in tables-1 and 2. The necessary data for calculation has been taken from literature[28-33]. The graphical representation of the computed values of available volumes from both the methods mentioned above, have been displayed in fig. 1(e) and fig. 2(c).

Available volume is found to increase with increasing temperature, which seems obvious, as there is increase in molecular motion and decrease in intermolecular attraction at higher temperatures. The values of available volumes from both the methods seem to be in close agreement. Best agreement is seen at moderate temperatures like 283.2K for acetone, 293.2K for methyl iodide, 293.2K for hexane etc. These results show the applicability of the thermoacoustical parameter for the computation of available volume in pure liquids.

In the binary liquid mixture of acetone and methyl iodide (as shown in table-2 and fig. 2.e), there is regular decrease in available volume with increase in mole fraction of methyl iodide. This result is obvious as methyl iodide as a pure component has lower value of available volume than that of acetone. The obvious results are obtained in other binary liquids mixtures also. In case of equimolar binary liquid mixtures of aromatic compounds with alkanes, regular increase in available volume with increasing molecular weight of alkane homologues is observed (Table-2.f). These results prove the applicability of thermoacoustical parameters for the computation of available volume in binary liquid mixtures.

7.4 References

1. Blackmann M, *Phil Mag*, **3** (1958) 831.
2. Batchelder D N, *J Phys Chem*, **41** (1964) 2327.
3. Wong C & Schule D E, *J Phys Chem Solids*, **29** (1968) 1309.
4. Knopoff L & Shapiro J N, *Phys Rev*, **B-1** (1970) 3893.
5. Rahim S A, Sriram M J & Ramchandra R B, *Ind J Pure & Appl Phys*, **14** (1963) 943.
6. Tandon U S & Pandey S K, *Phys Lett*, **41-A** (1972) 161.
7. Kor S K & Pandey S K, *Acustica*, **29** (1973) 63.
8. Pandey J D, *Acustica*, **34** (1975) 119.
9. Rao M R, *J Chem Phy*, **9** (1941) 682.
10. Wada Y, *J Phys Soc (Jap)*, **4** (1949) 280.
11. Sharma B K, *Acustica*, **45** (1980) 65.
12. Sharma B K, *Acustica*, **45** (1980) 135.
13. Carnevale E H & Litovitz T A, *J Acoust Soc Am*, **27** (1955) 547.
14. Coppens A B, Beyer R T, Seiden M B, Donohue J, Guepia F, Hodson R H & Townsend C, *J Acoust Soc Am*, **38** (1965) 797.
15. Sharma B K, *J Acoust Soc Am*, **73 (1)** (1983) 106.
16. Sharma B K, *Phys Lett*, **95A** (1983) 107.
17. Sharma B K, *J Acoust Soc Ind*, **4** (1984) 20.
18. Sharma B K, *J Acoust Soc Ind*, **4** (1984) 26.
19. Sharma B K, *Archives of Acoustics*, **11(2)** (1986) 183.
20. Sharma B K, *Ind J Pure & Appl Phys*, **25** (1987) 262.
21. Pandey J D, Tripathi N & Dubey G P, *Ind J Pure & Appl Phys*, **33** (1995) 7.
22. Sharma B K, *J Pure & Appl Ultrason*, **16** (1994) 51.
23. Pandey J D, Dubey G P & Dey R, *Acustica-acta acustica*, **83** (1997) 90.
24. Tabhane V A, Ghosh S & Agrawal S, *J Pure & Appl Ultrason*, **21** (1999) 122.
25. Cowan & Ball, *Can J Phys*, **58** (1980) 74.
26. Huggins M L, *J Chem Phys*, **5** (1937) 143.
27. Huggins M L, *J Chem Phys*, **15** (1947) 21.

28. Low D I R & Moelwyn-Hughes E A, *Proc Roy Soc A,* **267** (1962) 384.

29. Rajgopal E & Subrahmanyam S V, *J Chem Thermodyn*, **12** (1980) 797.

30. Sachdeva V K & Nanda V S, *J Chem Phys*, **75(9)** (1981) 4745.

31. Tardajos G, Aicart E, Costas M & Patterson D, *J Chem Soc Farad Trans*, **82** (1986) 2977.

32 Nath J, *J Chem Thermodyn*, **28** (1996) 481.

33. Hu J, Tamura K & Murakami S, *Fluid Phase Equilibria*, **134** (1997) 239.

Table - 1

Thermoacoustical, non-linear, anharmonic and volumetric properties of pure liquids

Liquids	T	α	V/ 10^{-6}	γ	V*/ 10^{-6}	C_1	β~	S_0	S^*	S_0^*	F	K	X	K''	K'	f	n_M	Γ_G	δ	B/A	V_a/ 10^{-6} m^3mol^{-1}	
	K	10^3K^{-1}	m^3mol^{-1}		m^3mol^{-1}																Eq 16	Eq 17
Cyclohexane	298.15	1 215	108.76	1.362	1 290	7.58	6.89	1.11	1.48	1.16	1 02	3.29	-0 50	0.31	3.60	0.217	1.33	1.00	5.09	7 42	23.65	22.53
	313 15	1.265	110 80	1.357	1.311	7.39	7.41	1.11	1 53	1.17	0.96	3.19	-0.48	0 39	3.58	0 218	1.32	0.90	4.86	7.44	24.18	24.53
	325.15	1 294	112.19	1.353	1 326	7 27	7.80	1.11	1.56	1.18	0.91	3.14	-0.47	0.44	3.57	0.219	1.31	0 84	4.71	7 46	24.53	26.17
Cyclohexanol	298 15	0.804	105 98	1.199	1 206	8.82	5.23	1.12	1.32	1.12	1.25	3.91	-0 57	-0.18	3.73	0 211	1.39	0.83	6.50	7 39	22 40	17 82
	313.15	0.823	107.28	1.200	1.219	8.56	5.45	1.12	1.34	1.13	1.21	3.78	-0.56	-0.08	3.70	0.213	1 38	0.78	6 21	7 37	22 82	19 20
	325 15	0 836	108.16	1.201	1.229	8.37	5.64	1.12	1.36	1.13	1.19	3.69	-0.55	-0.01	3.68	0 214	1.38	0 74	6.01	7 36	23.11	20 31
n-Pentane	283.15	1.517	113 46	1.333	1.332	7 23	7.94	1.11	1.57	1.18	0.90	3.12	-0 47	0.45	3 57	0.219	1.31	0.78	4 66	7.45	24.82	27.45
	288 15	1 548	114 31	1.335	1 341	7 17	8.21	1.10	1.59	1.19	0.87	3.08	-0.46	0.48	3.57	0.219	1.30	0.75	4.58	7 46	25.02	28.36
	293 15	1.579	115.22	1.335	1 351	7.11	8.49	1.10	1.62	1.19	0.84	3.06	-0 45	0.51	3.57	0.219	1.29	0 72	4.49	7.47	25 24	29 31
	303.15	1 637	117.11	1.330	1.370	7.01	9.07	1.09	1.66	1.20	0.78	3.01	-0 44	0.56	3.56	0.219	1.28	0.66	4 35	7.49	25.67	31 31
n-Hexane	293 15	1 374	130.39	1.297	1 315	7.35	7.51	1.11	1.54	1.17	0.94	3.18	-0.48	0.40	3.58	0 218	1 32	0 74	4.82	7 40	28.47	29.70
	313.15	1 454	134.02	1.289	1 347	7.14	8.36	1.10	1.61	1.19	0.85	3.07	-0 46	0 50	3 57	0.219	1.30	0.63	4.53	7 42	29 35	33 52
	333.15	1 526	137.56	1.270	1.376	6 98	9.29	1.09	1.68	1.20	0 76	2 99	-0.43	0.57	3.56	0 219	1.28	0 53	4.30	7 43	30 15	37.71
n-Heptane	293.15	1 250	146.66	1.273	1.293	7 55	6.96	1.11	1.49	1.16	1 01	3.28	0.50	0 32	3 60	0 218	1 33	0.75	5.06	7.37	31 91	30.68
	313 15	1 309	150 39	1.266	1.320	7.32	7.62	1.11	1.55	1.18	0.93	3.16	-0.48	0 42	3.58	0.218	1 31	0 65	4 77	7.38	32.86	34.44
	333.15	1 378	154 42	1.257	1.349	7.12	8.43	1 10	1.61	1.19	0.84	3.06	-0 46	0.50	3 57	0.219	1.29	0 56	4.51	7 39	33.82	38 61
	353 15	1.462	158.78	1.250	1.381	6 96	9.43	1.09	1.69	1.20	0.74	2.98	-0 43	0 58	3.56	0.219	1 27	0.48	4.27	7.42	34 80	43 27
n-Decane	293.15	1.026	194.99	1.220	1 250	8 06	6.02	1.12	1.40	1.14	1.13	3 53	-0 53	0.12	3.65	0 215	1 36	0.73	5 66	7 34	41 98	34.24
	313.15	1.069	199.09	1.218	1.272	7 77	6.49	1.12	1.45	1.15	1.07	3.38	-0 51	0.23	3.62	0.217	1.35	0 65	5.32	7.33	43.14	38.06
	333 15	1 114	203.42	1.215	1.296	7.52	7 03	1.11	1.49	1.17	1.00	3.26	-0.50	0.33	3.59	0 218	1.33	0.58	5.03	7 33	44 29	42 20
	353.15	1 162	208.20	1.205	1.320	7.32	7.63	1.11	1.55	1.18	0.93	3 16	-0 48	0 42	3.58	0 218	1 31	0.50	4.77	7 33	45 49	46.76
	363.15	1 187	210.61	1.200	1 332	7.23	7.96	1 10	1.57	1.18	0.89	3.11	-0 47	0 46	3 57	0 219	1.31	0 46	4.65	7.33	46.07	49.18
Acetone	253.20	1.332	69.61	1.405	1.274	7.75	6.53	1.12	1.45	1.16	1.06	3.37	-0 51	0 24	3.61	0.217	1 34	1 20	5.30	7 42	15 09	13.01
	263.20	1.344	70.53	1.396	1.285	7.63	6.77	1.11	1.47	1.16	1 03	3 32	-0 50	0 29	3 60	0.217	1.34	1 12	5.16	7 43	15 32	13 87
	273 20	1.361	71.48	1.394	1.296	7.52	7.04	1.11	1.50	1.17	1 00	3 26	-0.50	0.33	3.59	0.218	1 33	1 06	5.02	7 45	15 56	14.77
	283 20	1 380	72.47	1.385	1.308	7.41	7.32	1 11	1 52	1.17	0.97	3.21	-0 49	0.38	3 58	0 218	1.32	0 99	4.89	7.46	15.81	15.72
	293.20	1 398	73.48	1 375	1.320	7.32	7.62	1 11	1 55	1.18	0.93	3.16	-0 48	0.42	3 58	0 218	1 31	0.91	4 77	7.47	16 05	16.72
	303 20	1 416	74.53	1.363	1.331	7.23	7.93	1.11	1 57	1.18	0 90	3.12	-0 47	0 45	3.57	0.219	1 31	0 85	4 66	7.47	16.30	17.77

	308 20	1.435	75 07	1.362	1.339	7 18	8.15	1.10	1.59	1 19	0.87	3 09	-0 46	0 48	3 57	0 219	1 30	0 82	4 59	7 48	16 43	18 33
Methyl Iodide	253.20	1 167	59 40	1.534	1.246	8.11	5 95	1 12	1 39	1.14	1.14	3 56	-0 53	0.09	3 65	0.215	1 37	1.81	5 72	7 40	12 77	10 57
	263 20	1.184	60 10	1.544	1 257	7.96	6 17	1 12	1 42	1.15	1 11	3 48	-0 53	0.16	3.63	0 216	1 36	1 75	5 54	7 44	12 97	11 24
	273 20	1 200	60.82	1 550	1.268	7.82	6.40	1.12	1.44	1.15	1 08	3.41	-0.52	0.21	3.62	0 216	1 35	1 68	5.38	7 47	13.16	11.94
	283.20	1.214	61.56	1.548	1.278	7 70	6 62	1.11	1.46	1.16	1.05	3 35	-0.51	0.26	3.61	0 217	1 34	1.59	5 24	7.50	13.36	12.68
	293.20	1.229	62.32	1.544	1.289	7.59	6.86	1.11	1.48	1.16	1.02	3.29	-0 50	0.30	3.60	0.217	1 33	1 51	5 11	7.53	13.55	13 45
	303.20	1.242	63.10	1.526	1 299	7.49	7.11	1.11	1.50	1.17	0.99	3.25	-0 49	0.34	3.59	0.218	1.33	1.40	4 99	7.54	13 75	14.26
	308.20	1 254	63 49	1.524	1.305	7.44	7.26	1.11	1.52	1.17	0.97	3.22	-0.49	0 37	3.59	0 218	1 32	1 36	4.92	7.56	13.84	14 68
Oth Compds																						
n-Hexane	298.15	1.381	131.56	1.293	1.321	7 31	7.65	1.11	1.55	1 18	0.93	3.16	-0 48	0.42	3.58	0.218	1.31	0.71	4.76	7 40	28.75	30.68
n-Octane	298.15	1.160	163.53	1.250	1 280	7 69	6.65	1.11	1.46	1.16	1.05	3.34	-0.51	0 26	3.61	0 217	1 34	0 72	5 22	7.35	35.49	32.67
n-Decane	298 15	1 041	195.92	1 225	1.256	7.97	6.15	1.12	1 41	1.15	1.11	3.48	-0.53	0.15	3.64	0.216	1.36	0 72	5 56	7.34	42 26	35 15
n-Dodecane	298.15	0 978	228.58	1 213	1.243	8 15	5.90	1.12	1 39	1.14	1.15	3.58	-0.54	0.08	3.65	0.215	1 37	0.73	5.76	7.34	49 10	37.86
n-Tetradecane	298.15	0.931	261.34	1.204	1.233	8.31	5.71	1.12	1 37	1.14	1.17	3.65	-0.54	0.02	3.67	0.214	1.37	0.73	5.94	7 35	55.94	40.58
n-Hexadecane	298.15	0.902	294.05	1.200	1.227	8 41	5.60	1 12	1.36	1.13	1.19	3.71	-0.55	-0.02	3.68	0 214	1 38	0.74	6.05	7.36	62.78	43.55
Carb Tetr Chl	298.15	1.228	97.08	1.447	1.293	7.55	6 95	1.11	1.49	1.16	1 01	3.28	-0.50	0.32	3.60	0.218	1.33	1.22	5.06	7.48	21.12	19 96
Benzene	298 15	1 218	89.41	1.428	1 291	7.57	6.91	1.11	1.48	1.16	1.02	3 29	-0.50	0.31	3.60	0.218	1 33	1.18	5.09	7.46	19.45	18.14
p-xylene	298 15	1.019	123.92	1.329	1.252	8 03	6.06	1.12	1.41	1.14	1.13	3.51	-0.53	0.13	3.64	0.215	1.36	1.08	5.62	7 37	26.70	22.30
Toluene	298 15	1.086	106.88	1.350	1.265	7.85	6 34	1.12	1.43	1 15	1.09	3.43	-0 52	0.20	3 62	0 216	1 35	1.08	5.42	7.39	23.11	20.27
Dipropyl Ether	298.15	1 261	137.72	1.258	1.299	7.49	7.10	1.11	1.50	1.17	0.99	3.25	-0.49	0 34	3 59	0 218	1 33	0.69	4.99	7 36	30.00	30.21
Ethanol	298 15	1 125	58 68	1 202	1.273	7.76	6.50	1.12	1.45	1.15	1 07	3.38	-0.51	0 23	3.61	0.217	1 35	0.60	5.31	7.32	12.72	13 45
Ethyl Acetate	298.15	1 384	98 50	1.385	1.321	7.31	7.67	1.11	1.55	1.18	0.93	3.15	-0 48	0.42	3.58	0 219	1.31	0 93	4.76	7.48	21.52	22.02
Acetonitrile	298.15	1 372	52.85	1.418	1.319	7.32	7.61	1.11	1.55	1.18	0 93	3.16	-0 48	0.42	3 58	0.218	1 31	1.02	4 78	7 50	11 55	11.16
N,N-DMF	298 15	0.560	77 43	1 098	1 150	10 55	4 37	1.12	1 22	1.09	1.39	4.77	-0.61	-0.83	3 94	0.202	1.44	0 59	8.32	7 72	15 67	13.03
Dichloromethane	303.15	1.377	64.95	1.532	1.324	7 29	7.74	1.11	1.56	1.18	0.92	3.14	-0.47	0.43	3.58	0 219	1.31	1.27	4.73	7.61	14.20	15.40
1,2-dichloroethane	303.15	1.162	79 92	1.451	1.284	7.64	6.75	1.11	1.47	1.16	1.04	3.32	-0 51	0.28	3 60	0 217	1.34	1.28	5.17	7 46	17.36	16.43
Trichloroethene	303 15	1.139	90.52	1.430	1 279	7.69	6.64	1.11	1.46	1.16	1.05	3.34	-0.51	0.26	3.61	0.217	1 34	1.25	5.23	7.44	19.64	18.35
Tetrachloroethene	303 15	1.025	103.62	1.389	1.256	7.97	6.16	1.12	1.41	1.15	1.11	3.48	-0.53	0.15	3.64	0.216	1 36	1.25	5.55	7.39	22 35	18 89
Anisole	303.15	0 960	109.83	1.279	1.243	8.16	5.89	1.12	1.39	1 14	1 15	3 58	-0 54	0.08	3 66	0 215	1.37	0.96	5.77	7 35	23.59	19.02
Cyclohexane	303.15	1.233	109.41	1.375	1.298	7.51	7.07	1.11	1.50	1 17	1 00	3 25	-0.49	0.34	3.59	0 218	1.33	1.00	5.01	7.44	23.83	23.17
				Minimum Value:		6 96	4.37	1.09	1.22	1 09	0 74	2.98	-0.61	-0.83	3.56	0.20	1.27	0.46	4.27	7.32	11.55	10.57
				Maximum Value:		10.55	9.43	1.12	1.69	1.20	1.39	4.77	-0 43	0 58	3.94	0.22	1.44	1.81	8.32	7 72	62 78	49.18

Table - 2
Thermoacoustical, non-linear, anharmonic and volumetric properties in binary liquid mixtures

2. a) Binary liquid mixture: Cyclohexanol (1) + cyclohexane (2)

x_1	x_2	T	α	V/ 10^{-6}	V^-/ 10^{-6}	C_1	β^-	S_0	S^*	S_0^*	F	K	X	K''	K'	f	n_M	Γ_G	δ	B/A	V_a/ 10^{-6} m^3mol^{-1}	
		K	$10^{-3}K^{-1}$	m^3 mol^{-1}	m^3 mol^{-1}																Eq 16	Eq 17
0 0000	1.0000	298 15	1.215	108.76	1.290	7.58	6 89	1 11	1.48	1.16	1.02	3 29	-0 50	0 31	3.60	0.217	1.33	1.00	5.09	7.420	23.65	22 53
0.1977	0.8023	298.15	1.128	108.26	1.273	7.76	6 52	1.12	1.45	1.15	1.07	3.38	-0.51	0.24	3.61	0.217	1.35	0 91	5.31	7 373	23.46	21 43
0.3178	0.6822	298 15	1.077	107.92	1.263	7.88	6.30	1.12	1.43	1.15	1.09	3.44	-0.52	0 19	3 63	0.216	1.35	0 90	5.45	7.362	23 33	20.81
0 4185	0 5815	298.15	1.047	107.60	1.257	7.95	6.18	1 12	1.42	1.15	1.11	3.48	-0.53	0 16	3.63	0.216	1.36	0.89	5.54	7.355	23.22	20.31
0.5050	0.4950	298.15	1.018	107.34	1.251	8.03	6.06	1.12	1.40	1.14	1.13	3.52	-0 53	0.13	3.64	0 215	1.36	0 87	5.63	7.351	23.12	19 89
0 6828	0.3172	298 15	0 968	106.79	1.241	8.18	5 86	1.12	1 38	1.14	1.15	3.59	-0 54	0.07	3 66	0.215	1.37	0 88	5.80	7.351	22 92	19.09
0.7871	0.2129	298.15	0 911	106.49	1.229	8 38	5.63	1.12	1 36	1.13	1.19	3.69	-0.55	-0 01	3.68	0.214	1.38	0.86	6.02	7 356	22.76	18.65
0.9001	0.0999	298 15	0.860	106.20	1 218	8 58	5 44	1.12	1 34	1.13	1.21	3.79	-0.56	-0 09	3.70	0.213	1.39	0 85	6.23	7.368	22.58	18.20
1 0000	0 0000	298.15	0.804	105.98	1.206	8.82	5 23	1.12	1.32	1.12	1.25	3.91	-0 57	-0.18	3.73	0 211	1.39	0.85	6.50	7 389	22.40	17 82
0.0000	1 0000	323 15	1.294	112.19	1.325	7.28	7.75	1 11	1.56	1.18	0.92	3.14	-0.47	0.43	3.57	0.219	1.31	0.84	4.72	7.456	24.52	25.94
0.1977	0.8023	323 15	1 156	111.44	1 297	7 51	7 06	1 11	1 50	1.17	1 00	3.25	-0 49	0.34	3.59	0.218	1.33	0.74	5.01	7.370	24 27	24 59
0.3178	0 6822	323.15	1.114	110.94	1.289	7 59	6.86	1.11	1.48	1.16	1 02	3.30	-0 50	0.30	3.60	0.217	1.33	0 74	5.11	7.360	24.12	23 82
0 4185	0.5815	323.15	1.075	110.51	1.281	7.68	6.68	1.11	1.46	1.16	1 04	3.34	-0 51	0.27	3.61	0.217	1.34	0.74	5.21	7.352	23.99	23 20
0.5050	0.4950	323.15	1.045	110.14	1.274	7.74	6.54	1.12	1 45	1.16	1.06	3.37	-0 51	0.24	3 61	0.217	1.34	0.72	5.29	7.344	23.87	22 69
0.6828	0.3172	323.15	0.986	109.40	1.262	7.90	6.27	1.12	1.42	1.15	1.10	3 45	-0.52	0.18	3.63	0.216	1.35	0.74	5.47	7.342	23.64	21 71
0.7871	0.2129	323.15	0.939	108.98	1.251	8.03	6.06	1.12	1.40	1.14	1.13	3.52	-0.53	0 13	3.64	0.215	1.36	0 75	5.63	7.342	23.47	21.17
0.9001	0.0999	323.15	0.885	108.54	1.239	8.21	5.82	1.12	1.38	1 14	1.16	3 61	-0.54	0 06	3.66	0.215	1.37	0 74	5.83	7.347	23.28	20 62
1.0000	0.0000	323 15	0.836	108.16	1.228	8.40	5.61	1 12	1.36	1 13	1 19	3.70	-0 55	-0 02	3.68	0.214	1.38	0 74	6.03	7.357	23.10	20.15

2. b) Binary liquid mixture: Acetone (1) + methyl iodide (2)

x_1	x_2	T	α	V/ 10^{-6}	$\bar{V}$/ 10^{-6}	C_l	β^-	S_0	S^*	S_0^*	F	K'	X	K''	K'	f	n_M	Γ_G	δ	B/A	V_a/ 10^{-6} m^3mol^{-1}	
		K	$10^{-3}K^{-1}$	m^3 mol^{-1}	m^3 mol^{-1}																Eq 16	Eq 17
0 0000	1 0000	253 20	1.167	59.40	1.246	8 11	5.95	1.12	1.39	1.14	1 14	3.56	-0.53	0.09	3.65	0.215	1.37	1 81	5.72	7.403	12.77	10.57
0.2000	0 8000	253.20	1.269	61.76	1.263	7.87	6.30	1.12	1.43	1 15	1.09	3.44	-0.52	0 19	3.63	0 216	1.35	1.66	5.45	7 454	13.35	11.10
0 4000	0 6000	253 20	1 298	63.95	1.268	7.81	6 41	1.12	1.44	1.15	1.08	3.41	-0.52	0 21	3 62	0.216	1.35	1.51	5.38	7.451	13.84	11.60
0 6000	0 4000	253.20	1.314	65.95	1.271	7.78	6.46	1.12	1.44	1.15	1.07	3 39	-0.52	0.23	3.62	0.217	1.35	1.37	5.34	7.440	14.28	12.08
0 8000	0 2000	253.20	1.324	68.06	1.273	7.76	6.50	1.12	1.45	1.15	1.07	3.38	-0 51	0.23	3.62	0.217	1.35	1.28	5.32	7 430	14 75	12 59
1 0000	0 0000	253.20	1.332	69 61	1.274	7.75	6.53	1.12	1.45	1.16	1.06	3 37	-0.51	0.24	3.61	0.217	1.34	1 20	5.30	7.421	15.09	13 01
0.0000	1.0000	263.20	1.184	60.10	1.257	7.96	6.17	1.12	1.42	1.15	1.11	3 48	-0.53	0.16	3.63	0 216	1 36	1.75	5.54	7.438	12.97	11.24
0.2000	0.8000	263.20	1 277	62.50	1 273	7 76	6.51	1.12	1.45	1.15	1.07	3.38	-0.51	0.24	3.61	0 217	1.35	1 58	5.31	7.479	13.54	11.80
0.4000	0.6000	263.20	1.310	64 75	1.279	7.69	6.64	1.11	1.46	1.16	1.05	3 35	-0.51	0.26	3.61	0 217	1.34	1.42	5.23	7 473	14.05	12 35
0.6000	0.4000	263.20	1.326	66.85	1.282	7.66	6.70	1.11	1.47	1.16	1.04	3.33	-0.51	0.27	3.61	0.217	1 34	1.29	5.20	7.458	14.51	12.88
0.8000	0 2000	263 20	1.335	68.95	1.283	7.65	6.73	1.11	1.47	1.16	1.04	3.32	-0.51	0.28	3.60	0 217	1.34	1.19	5.18	7.443	14.98	13.42
1.0000	0.0000	263.20	1 344	70 53	1.285	7.63	6 77	1 11	1.47	1.16	1.03	3.32	-0.50	0 29	3 60	0 217	1.34	1.12	5.16	7 433	15 32	13.87
0.0000	1.0000	273 20	1 200	60.82	1.268	7.82	6.40	1.12	1.44	1.15	1.08	3.41	-0 52	0.21	3.62	0.216	1.35	1.68	5.38	7 473	13.16	11 94
0.2000	0 8000	273.20	1.282	63 29	1.282	7.66	6.72	1.11	1 47	1.16	1.04	3 33	-0 51	0.28	3.60	0.217	1.34	1 50	5 19	7.502	13.74	12.55
0.4000	0 6000	273.20	1.316	65 60	1.288	7.59	6 85	1.11	1.48	1.16	1.02	3.30	-0.50	0.30	3.60	0 217	1.33	1.33	5.11	7 487	14 26	13.14
0 6000	0.4000	273.20	1.333	67.75	1.291	7 56	6 92	1.11	1.49	1.16	1.01	3 28	-0.50	0 31	3.60	0.218	1.33	1 21	5.08	7 469	14 74	13.71
0.8000	0.2000	273.20	1.347	69 85	1.294	7.54	6.98	1.11	1.49	1.16	1.01	3.27	-0.50	0.32	3.59	0 218	1.33	1.12	5.05	7.456	15.20	14.28
1.0000	0 0000	273.20	1 361	71.48	1.296	7.52	7.04	1.11	1.50	1.17	1 00	3.26	-0.50	0.33	3.59	0.218	1.33	1.06	5.02	7.448	15.56	14.77
0.0000	1.0000	283.20	1.214	61.56	1.278	7.70	6.62	1.11	1.46	1.16	1 05	3 35	-0 51	0.26	3.61	0.217	1.34	1.59	5.24	7.502	13 36	12.68
0 2000	0 8000	283.20	1.292	64.08	1.293	7.55	6.95	1.11	1.49	1.16	1.01	3 28	-0 50	0.32	3.60	0.218	1.33	1.40	5.07	7.518	13.94	13.33
0.4000	0 6000	283.20	1.323	66.45	1.298	7.50	7 08	1.11	1.50	1.17	0.99	3.25	-0.49	0.34	3.59	0.218	1.33	1.24	5 00	7 500	14.47	13.97
0.6000	0.4000	283.20	1.342	68.66	1.301	7.47	7.16	1.11	1.51	1 17	0.98	3 24	-0.49	0 35	3.59	0.218	1.33	1.13	4.96	7 482	14.96	14.58
0.8000	0 2000	283.20	1.361	70 80	1.305	7 44	7 24	1.11	1.51	1.17	0 98	3 22	-0.49	0.37	3.59	0 218	1.32	1.04	4.93	7 467	15.44	15.19
1.0000	0.0000	283 20	1.380	72.47	1 308	7.41	7.32	1.11	1.52	1 17	0 97	3 21	-0.49	0 38	3.58	0.218	1.32	0.99	4.89	7 459	15.81	15.72
0.0000	1.0000	303.50	1.242	63.10	1.299	7 49	7 11	1 11	1.50	1.17	0 99	3 24	-0.49	0.35	3 59	0 218	1 33	1 40	4 99	7 544	13.75	14 28

0.2000	0 8000	303.50	1 306	65.80	1.312	7.38	7.41	1.11	1 53	1.17	0.96	3.19	-0 48	0 39	3.58	0.218	1.32	1.22	4 86	7.540	14.36	15 05
0.4000	0.6000	303 50	1 339	68 24	1.318	7.34	7.57	1.11	1.54	1.18	0.94	3.17	-0.48	0 41	3 58	0.218	1 32	1.08	4.79	7.516	14.90	15 77
0.6000	0 4000	303 50	1.364	70 53	1.322	7.30	7.69	1.11	1.55	1.18	0.92	3.15	-0.48	0.43	3 58	0.219	1 31	0.97	4 75	7.493	15.41	16.48
0.8000	0.2000	303.50	1.390	72.72	1.327	7.27	7.81	1.11	1.56	1.18	0.91	3.13	-0.47	0.44	3.57	0.219	1.31	0.90	4.70	7 481	15.90	17.18
1.0000	0.0000	303.50	1 416	74.53	1.332	7.23	7.94	1.11	1.57	1.18	0.90	3 12	-0.47	0.46	3 57	0.219	1.31	0 84	4 66	7 474	16.30	17.80

2. c) Binary liquid mixture: Ethyl acetate (1) + benzene (2)

x_1	x_2	T	α	$V/10^{-6}$	$V^{-}/10^{-6}$	C_1	β^{-}	S_0	S^{*}	S_0^{*}	F	K	X	K''	K'	f	n_M	Γ_G	δ	B/A	$V_s/10^{-6}$ m^3mol^{-1}	
		K	$10^{-3}K^{-1}$	m^3 mol^{-1}	m^3 mol^{-1}																Eq 16	Eq 17
0.0000	1.0000	298.15	1.242	89.40	1.295	7.53	7.01	1.11	1.49	1.17	1.00	3.26	-0 50	0.33	3 59	0 218	1.33	1.20	5 03	7 481	19.46	18 14
0.0245	0.9755	298 15	1.245	89.64	1.296	7.52	7 03	1.11	1.49	1.17	1.00	3.26	-0.50	0.33	3.59	0.218	1.33	1.20	5 03	7.481	19.52	18.22
0.0503	0.9497	298.15	1.249	89.89	1.297	7.52	7.04	1.11	1.50	1.17	1.00	3.26	-0.50	0 33	3.59	0.218	1.33	1.19	5.02	7.482	19.57	18.32
0.0998	0.9002	298 15	1.257	90.37	1.298	7.50	7.08	1.11	1.50	1.17	0.99	3 25	-0.49	0.34	3 59	0.218	1 33	1.17	5.00	7.482	19.68	18.50
0.1495	0.8505	298.15	1.265	90.84	1.300	7.49	7.12	1.11	1.50	1.17	0.99	3.24	-0.49	0.35	3.59	0.218	1.33	1.16	4.98	7.483	19.79	18.68
0.2498	0.7502	298.15	1.280	91.78	1.302	7.46	7.18	1.11	1.51	1 17	0.98	3.23	-0.49	0.36	3.59	0.218	1.33	1.13	4.95	7.483	20.00	19.06
0.3003	0.6997	298.15	1.287	92.25	1.304	7.45	7.22	1.11	1.51	1.17	0.98	3.23	-0.49	0 36	3.59	0 218	1.32	1.11	4.94	7 483	20 11	19.25
0.3987	0.6013	298.15	1 302	93.16	1.307	7.43	7.28	1.11	1 52	1.17	0.97	3.21	-0 49	0 37	3.59	0 218	1.32	1.08	4.91	7 483	20.32	19.62
0.4439	0.5561	298.15	1.308	93.57	1.308	7.42	7.31	1.11	1.52	1.17	0.97	3.21	-0.49	0.38	3.58	0.218	1.32	1.07	4.90	7.483	20 41	19.79
0 5504	0.4496	298 15	1 324	94.53	1.311	7.39	7 39	1.11	1.53	1.17	0.96	3.20	-0.48	0.39	3 58	0.218	1 32	1 04	4.87	7.483	20.63	20 20
0.6005	0.3995	298.15	1.331	94.99	1.312	7.38	7.42	1.11	1.53	1 17	0.95	3.19	-0.48	0.39	3.58	0.218	1.32	1.03	4.85	7 482	20.73	20.40
0.6501	0.3499	298.15	1.337	95.43	1.313	7.37	7.45	1.11	1.53	1.17	0.95	3.19	-0.48	0.39	3.58	0.218	1.32	1.02	4.84	7.482	20.83	20.60
0.7494	0.2506	298.15	1.351	96.31	1.316	7.35	7.51	1.11	1.54	1.17	0.94	3.18	-0.48	0.40	3.58	0.218	1 32	0.99	4.82	7 481	21.03	20.99
0.7994	0.2006	298.15	1.358	96.75	1.317	7.34	7.54	1.11	1.54	1.18	0.94	3.17	-0.48	0.41	3.58	0.218	1.32	0.98	4.80	7.481	21.13	21.19
0.8504	0.1496	298 15	1.365	97.20	1.318	7.33	7.58	1.11	1.54	1.18	0.94	3.17	-0.48	0.41	3.58	0.218	1.31	0 97	4 79	7.480	21.23	21.40
0.9002	0.0998	298.15	1.371	97.64	1.319	7.32	7.60	1.11	1.55	1.18	0.93	3 16	-0.48	0.42	3.58	0.218	1.31	0 95	4.78	7.479	21.33	21.61
0.9506	0.0494	298.15	1.377	98.08	1.320	7.32	7.63	1.11	1.55	1.18	0.93	3.16	-0.48	0 42	3 58	0.218	1 31	0.94	4.77	7.478	21 43	21.81
0.9748	0.0252	298 15	1.381	98.28	1.321	7.31	7.65	1.11	1.55	1.18	0.93	3.16	-0.48	0 42	3.58	0.218	1.31	0 94	4 76	7.479	21.47	21.91
1.0000	0.0000	298.15	1 384	98.50	1.321	7.31	7.67	1.11	1.55	1.18	0.93	3.15	-0 48	0.42	3 58	0.219	1.31	0.93	4.76	7.479	21.52	22.02

2. d) Binary liquid mixture: Ethyl acetate (1) + ethanol (2)

x_1	x_2	T / K	α / $10^{-3}K^{-1}$	V / 10^{-6} m^3 mol^{-1}	$\bar{V}$ / 10^{-6} m^3 mol^{-1}	C_t	β^-	S_0	S^*	S_0^*	F	K	X	K''	K'	f	n_M	Γ_G	δ	B/A	V_a / 10^{-6} m^3mol^{-1} Eq 16	V_a / 10^{-6} m^3mol^{-1} Eq 17
0.0000	1.0000	298 15	1.125	58 68	1.273	7.76	6.50	1.12	1.45	1.15	1.07	3.38	-0.51	0.23	3.61	0.217	1.35	0.60	5.31	7.32	12.72	13.45
0 0248	0.9752	298 15	1 136	59.68	1.275	7.74	6.55	1.12	1.45	1.16	1 06	3.37	-0.51	0.24	3.61	0.217	1.34	0 61	5.29	7.33	12 94	13 67
0.0497	0.9503	298.15	1.146	60.69	1.277	7.72	6.59	1 12	1.46	1.16	1.06	3 36	-0.51	0 25	3.61	0.217	1.34	0 62	5.26	7.33	13.16	13.89
0.0999	0.9001	298 15	1 166	62.72	1 281	7.67	6 68	1.11	1.46	1.16	1.04	3.34	-0 51	0.27	3.61	0.217	1.34	0.64	5.21	7.33	13.62	14.34
0.1509	0.8491	298.15	1.185	64.77	1 284	7.63	6.76	1.11	1.47	1.16	1.03	3.32	-0.50	0.29	3.60	0.217	1 34	0.67	5.16	7.34	14.07	14.79
0.1992	0 8008	298.15	1.202	66.71	1.288	7.60	6 84	1.11	1.48	1.16	1.02	3 30	-0.50	0.30	3.60	0.217	1 34	0.68	5.12	7.35	14.50	15.22
0.2503	0.7497	298 15	1.219	68 76	1.291	7.57	6.91	1.11	1.48	1.16	1.02	3.28	-0.50	0.31	3.60	0.218	1 33	0.70	5.08	7.35	14.96	15.66
0 3003	0.6997	298.15	1.234	70 77	1.294	7.54	6.98	1.11	1.49	1.16	1.01	3.27	-0 50	0.32	3.59	0.218	1.33	0 72	5.05	7.36	15.40	16 10
0 3480	0.6520	298.15	1 248	72.67	1 296	7.52	7.04	1.11	1.50	1.17	1.00	3.26	-0.50	0.33	3.59	0.218	1 33	0.74	5.02	7.37	15.82	16 51
0.3949	0.6051	298 15	1 261	74.55	1 299	7.49	7.10	1.11	1.50	1.17	0.99	3.25	-0.49	0 34	3.59	0.218	1 33	0 75	4.99	7.38	16.24	16.92
0 4508	0 5492	298.15	1.276	76 78	1.302	7.47	7.17	1.11	1.51	1.17	0.98	3.23	-0.49	0.35	3.59	0.218	1.33	0 77	4.96	7.38	16.73	17.40
0 4989	0 5011	298 15	1.288	78.70	1 304	7.45	7.22	1.11	1 51	1.17	0.98	3.22	-0 49	0.36	3.59	0 218	1 32	0.79	4.94	7 39	17.16	17 81
0 5397	0.4603	298.15	1 298	80 33	1.306	7 43	7 27	1.11	1.52	1.17	0.97	3.22	-0.49	0.37	3.59	0.218	1.32	0.80	4.92	7.40	17.52	18 16
0 5987	0 4013	298.15	1.310	82.68	1.308	7.41	7.32	1 11	1.52	1.17	0.97	3.21	-0.49	0.38	3.58	0.218	1.32	0.82	4 89	7.41	18.04	18.67
0 6501	0.3499	298.15	1 320	84.72	1.310	7.40	7.37	1.11	1.52	1.17	0.96	3.20	-0.49	0.38	3.58	0.218	1.32	0.83	4.87	7.42	18.49	19 10
0 7015	0 2985	298.15	1.330	86.76	1.312	7.38	7.41	1.11	1.53	1.17	0.96	3.19	-0.48	0.39	3.58	0.218	1.32	0.85	4.86	7.43	18.94	19.54
0 7468	0 2532	298.15	1.339	88.55	1.313	7.37	7.45	1.11	1.53	1.17	0.95	3.19	-0.48	0.40	3.58	0.218	1.32	0 86	4.84	7.43	19.33	19.92
0.7981	0.2019	298.15	1.348	90.58	1.315	7.36	7.50	1.11	1.54	1.17	0.95	3 18	-0.48	0.40	3.58	0.218	1.32	0.88	4.82	7.44	19.78	20 35
0 8499	0.1501	298.15	1.359	92.60	1.317	7.34	7.55	1.11	1.54	1.18	0.94	3.17	-0.48	0.41	3 58	0.218	1.32	0.89	4.80	7 45	20.22	20.78
0.9501	0.0499	298.15	1.377	96.55	1.320	7.32	7.63	1.11	1.55	1.18	0.93	3.16	-0.48	0.42	3.58	0.218	1.31	0.92	4.77	7 47	21.09	21.61
0.9739	0.0261	298.15	1.380	97.48	1.321	7.31	7.65	1.11	1.55	1.18	0.93	3.16	-0.48	0.42	3.58	0.218	1 31	0.93	4.76	7.47	21.30	21 81
1.0000	0.0000	298.15	1.384	98 50	1.321	7.31	7.67	1.11	1.55	1.18	0.93	3.15	-0.48	0.42	3.58	0.219	1.31	0.93	4.76	7.48	21.52	22.02

2. e) Binary liquid mixture: Acetonitrile (1) + N,N-DMF (2)

x_1	x_2	T	α	V/ 10^{-6}	V^E/ 10^{-6}	C_1	β	S_0	S*	S_0*	F	K	X	K''	K'	f	n_M	Γ_G	δ	B/A	V_a/ 10^{-6} m^3mol^{-1}	
		K	$10^{-3}K^{-1}$	m^3 mol^{-1}	m^3 mol^{-1}																Eq 16	Eq 17
0.0000	1 0000	298.15	0.560	77.43	1 150	10.55	4.37	1 12	1.22	1 09	1.39	4.77	-0.61	-0.83	3.94	0.202	1.44	0.59	8.32	7.72	15.67	13.03
0 0114	0 9886	298.15	0.567	77.15	1.152	10.47	4.39	1.12	1.23	1.09	1.38	4.74	-0.61	-0.80	3.93	0.203	1.44	0.60	8.25	7.71	15.64	13.02
0.0144	0 9856	298.15	0 569	77.08	1.152	10.45	4.40	1.12	1.23	1 09	1.38	4.73	-0.61	-0.80	3.93	0.203	1.44	0 60	8.23	7.70	15.63	13 01
0 0841	0.9159	298 15	0.609	75.33	1.162	10.08	4.53	1.12	1.24	1.10	1.36	4.54	-0.60	-0.66	3.88	0.205	1.43	0.63	7.84	7.62	15.42	12 90
0 1030	0 8970	298.15	0 619	74.86	1 164	10.00	4.57	1.12	1.25	1.10	1.35	4 50	-0.60	-0 62	3.87	0.205	1.43	0.63	7.75	7.60	15 36	12.87
0 1527	0.8473	298.15	0.650	73.62	1.171	9.75	4.67	1.12	1.26	1.10	1.34	4 38	-0.59	-0.53	3.84	0.206	1.42	0 66	7.49	7.55	15 20	12.79
0 2045	0.7955	298.15	0 681	72 33	1.178	9.53	4.78	1.12	1.27	1.11	1.32	4.26	-0.59	-0 45	3 82	0.208	1.42	0.68	7.26	7.51	15.02	12.70
0.2683	0.7317	298.15	0.723	70.74	1.188	9.26	4.93	1.12	1.29	1 11	1.29	4.13	-0.58	-0 35	3.78	0.209	1 41	0.71	6.97	7.46	14.79	12.59
0.3132	0.6868	298.15	0.753	69.63	1.195	9.09	5.04	1.12	1 30	1 12	1 28	4.04	-0.58	-0.28	3.76	0.210	1.40	0.73	6.79	7.43	14 62	12.51
0 3697	0.6303	298.15	0.793	68.22	1.204	8.88	5.19	1.12	1.32	1 12	1.25	3 94	-0 57	-0 20	3.74	0.211	1.40	0.75	6.56	7.40	14.40	12 41
0.4759	0.5241	298 15	0.871	65.60	1 221	8.53	5.48	1.12	1.35	1.13	1 21	3.77	-0.55	-0.07	3 70	0.213	1 38	0.80	6.18	7.37	13.97	12.22
0 5318	0.4682	298 15	0.915	64.22	1 230	8.36	5.65	1.12	1.36	1.13	1.18	3.68	-0.55	0.00	3.68	0.214	1.38	0.82	6.00	7 35	13.73	12.11
0.5760	0.4240	298.15	0 951	63.13	1.238	8.24	5.79	1.12	1.38	1.14	1.16	3.62	-0.54	0.05	3 66	0.214	1.37	0.84	5.86	7.35	13 53	12.03
0.6348	0 3652	298.15	1.001	61.69	1 248	8.08	5.99	1.12	1.40	1.14	1.14	3.54	-0 53	0.11	3.65	0.215	1.36	0.87	5 68	7.35	13.27	11.92
0.6877	0.3123	298.15	1.047	60.40	1.257	7.95	6.18	1.12	1.42	1.15	1.11	3.48	-0.53	0.16	3.63	0.216	1 36	0.89	5.54	7.36	13.03	11.81
0 7431	0.2569	298 15	1.099	59.05	1.268	7.82	6.39	1.12	1.44	1 15	1.08	3.41	-0.52	0.21	3.62	0 216	1.35	0.91	5.39	7.37	12.78	11.70
0.7907	0.2093	298 15	1.145	57.89	1.277	7.72	6.59	1.12	1.46	1 16	1.06	3.36	-0 51	0.25	3.61	0.217	1.34	0.93	5.26	7.38	12.56	11 60
0.8453	0.1547	298.15	1 200	56.56	1.287	7.61	6.83	1.11	1.48	1.16	1.03	3.30	-0.50	0 30	3.60	0 217	1 34	0.96	5.13	7.40	12.29	11.49
0.8954	0.1046	298.15	1.254	55.36	1.298	7.51	7.07	1.11	1.50	1.17	1.00	3.25	-0.49	0 34	3.59	0.218	1.33	0 98	5.01	7.43	12.06	11.39
0.9486	0.0515	298 15	1.312	54.08	1.308	7.41	7.33	1.11	1.52	1.17	0.96	3.21	-0 49	0 38	3.58	0 218	1 32	1.00	4.89	7.46	11 80	11.27
0.9724	0.0276	298.15	1.339	53.51	1.313	7.37	7.45	1.11	1.53	1.17	0.95	3.19	-0.48	0.40	3.58	0 218	1 32	1.01	4.84	7.48	11 68	11 22
1.0000	0.0000	298.15	1.372	52.85	1.319	7.32	7.61	1.11	1.55	1.18	0.93	3.16	-0.48	0 42	3.58	0.218	1.31	1.02	4.78	7.50	11.55	11 16

2. f) Binary liquid mixture: Equimolar mixture of aromatic compounds + n-alkanes

Liquid Mixtures	T	α	V/ 10^{-6}	V^{-}/ 10^{-6}	C_1	β^{-}	S_0	S^*	S_0^*	F	K	X	K''	K'	f	n_M	Γ_G	δ	B/A	V_s/ 10^{-6} m^3mol^{-1}	
	K	$10^{-3}K^{-1}$	m^3 mol^{-1}	m^3 mol^{-1}																Eq 16	Eq 17
Benzene+C6	298 15	1.305	110.88	1.307	7.42	7.30	1.11	1.52	1.17	0.97	3.21	-0.49	0.37	3.58	0.218	1.32	0.87	4.90	7.42	24 18	24.05
Benzene+C8	298 15	1.178	127.19	1.283	7.65	6.73	1.11	1.47	1.16	1.04	3.32	-0.51	0.28	3.60	0.217	1.34	0 85	5.18	7.37	27.62	25.60
Benzene+C10	298 15	1 099	143.52	1.268	7.82	6.39	1.12	1.44	1.15	1.08	3.41	-0 52	0.21	3.62	0.216	1.35	0.84	5.39	7.36	31.06	27.32
Benzene+C12	298.15	1.041	159.93	1.256	7.97	6.15	1.12	1.41	1.15	1 11	3 48	-0.53	0.15	3.64	0.216	1.36	0.82	5.56	7.35	34.50	29.15
Benzene+C14	298 15	0.991	176.40	1.246	8 11	5.95	1.12	1.39	1.14	1.14	3 56	-0.53	0.09	3.65	0.215	1.37	0.80	5.72	7.35	37.93	31.01
Benzene+C16	298.15	0 960	192.85	1.239	8.21	5.82	1.12	1.38	1.14	1.16	3.60	-0 54	0.06	3.66	0.215	1.37	0.80	5 83	7.35	41.37	32.90
Tolune+C6	298.15	1.231	119.19	1.293	7 55	6.96	1.11	1.49	1.16	1.01	3.27	-0.50	0.32	3.60	0.218	1.33	0.86	5.06	7.39	25.94	24.92
Toluene+C8	298.15	1.128	135.45	1.273	7.76	6.52	1.12	1.45	1.15	1.07	3.38	-0.51	0.24	3.61	0.217	1.35	0 83	5.31	7.36	29.35	26.35
Toulene+C10	298 15	1.057	151.77	1.259	7.93	6.22	1.12	1.42	1.15	1.10	3.46	-0 52	0.17	3.63	0.216	1.36	0 83	5.51	7.35	32.77	27.98
Toluene+C12	298 15	1.011	168.18	1.250	8.05	6.03	1.12	1.40	1.14	1 13	3 53	-0 53	0.12	3.64	0.215	1.36	0.82	5.65	7 35	36.21	29.73
Toluene+C14	298.15	0 972	184 53	1.242	8 17	5.87	1.12	1.39	1.14	1.15	3 59	-0 54	0.07	3.66	0.215	1 37	0.81	5 78	7 35	39 62	31.50
Toluene+C16	298.15	0.943	200.99	1.236	8.26	5.76	1.12	1.37	1.14	1.17	3 63	-0.54	0.03	3.67	0.214	1.37	0 80	5.89	7.35	43.06	33.32
Chlorobenzene+C6	298.15	1.171	116.41	1.282	7.66	6.70	1.11	1.47	1.16	1.04	3.33	-0.51	0.27	3.61	0.217	1.34	0 89	5.20	7.38	25.28	23.19
Chlorobenzene+C8	298.15	1 084	132.77	1.265	7.86	6 33	1.12	1.43	1.15	1.09	3.43	-0.52	0.20	3.62	0.216	1.35	0 88	5 43	7.36	28.71	24.70
Chlorobenzene+C10	298.15	1.023	149.24	1.252	8.02	6 08	1.12	1.41	1.14	1.12	3 51	-0.53	0.13	3.64	0.215	1.36	0.85	5.61	7.35	32.16	26.37
Chlorobenzene+C12	298.15	0 978	165.62	1.243	8.15	5.90	1.12	1.39	1.14	1.15	3 58	-0 54	0.08	3.65	0.215	1.37	0.84	5.76	7 35	35.58	28.11
Chlorobenzene+C14	298.15	0.946	182.10	1.237	8.25	5.77	1.12	1.38	1.14	1.17	3.63	-0.54	0.04	3.67	0.214	1.37	0 83	5.88	7.35	39.02	29.89
Chlorobenzene+C16	298.15	0 921	198.45	1.231	8.34	5.67	1.12	1.37	1.13	1 18	3 67	-0 55	0.01	3.68	0.214	1.38	0 82	5.98	7.35	42.44	31.68

Fig. 1: Pseudo-Gruneisen parameter, Anderson-Gruneisen parameter and available volume in some pure liquids

Fig. 1. a): Pseudo-Gruneisen parameter in alkanes at 298.15K

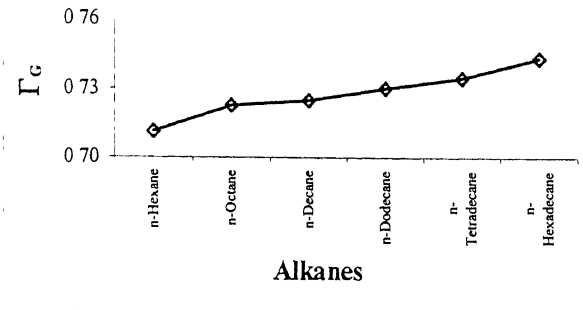


Fig. 1. b): Anderson-Gruneisen parameter in alkanes at 298.15K

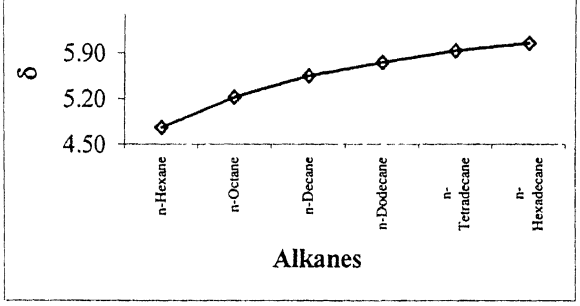


Fig. 1. c): Pseudo-Gruneisen parameter in acetone at varying temperature

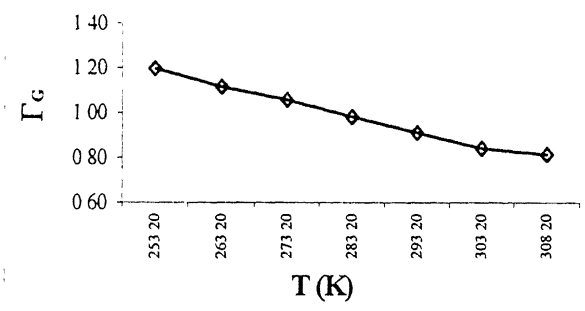


Fig. 1. d): Anderson-Gruneisen parameter in acetone at varying temperature

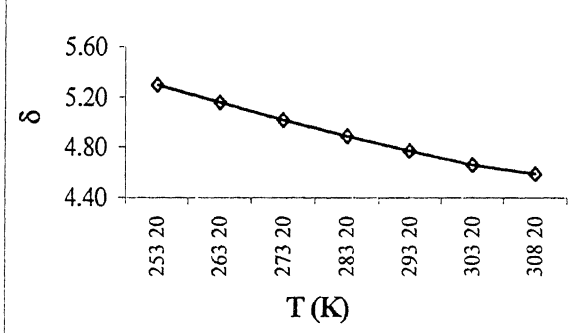


Fig. 1. e): Available volume in acetone and methyl iodide at varying temperatures

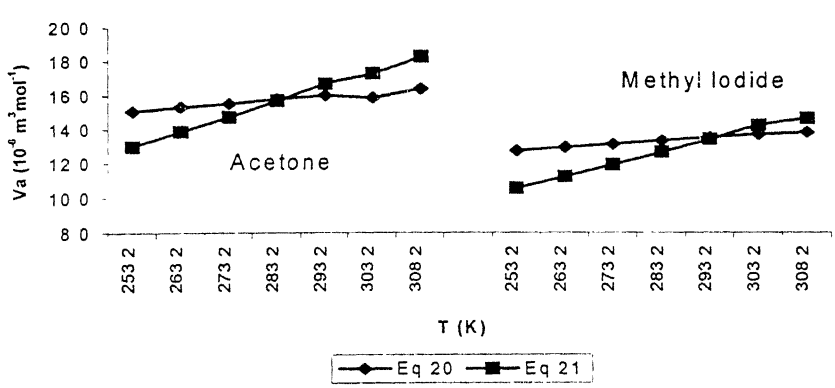


Fig. 2: Anderson-Gruneisen parameter, non-linear parameter and volumetric properties in binary liquid mixtures

Fig. 2. a): Anderson-Gruneisen parameter in equimolar mixture of aromatic compounds+n-alkanes at 298.15K

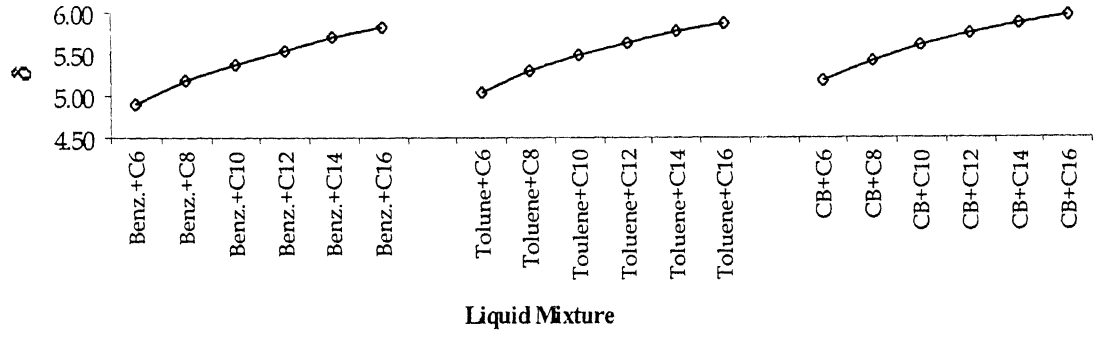


Fig. 2. b): B/A in liquid mixture benzene (1) + N,N-DMF (2) at 298.15K

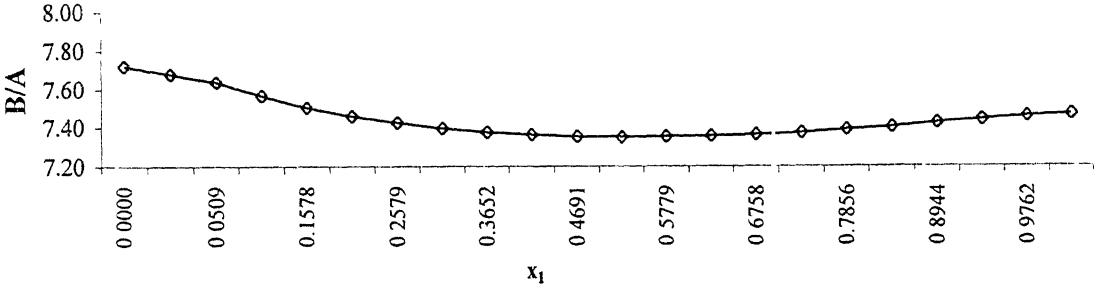


Fig. 2. c): Available Volume in Binary Liquid Mixture Acetone (1) + Methyl Iodide (2)

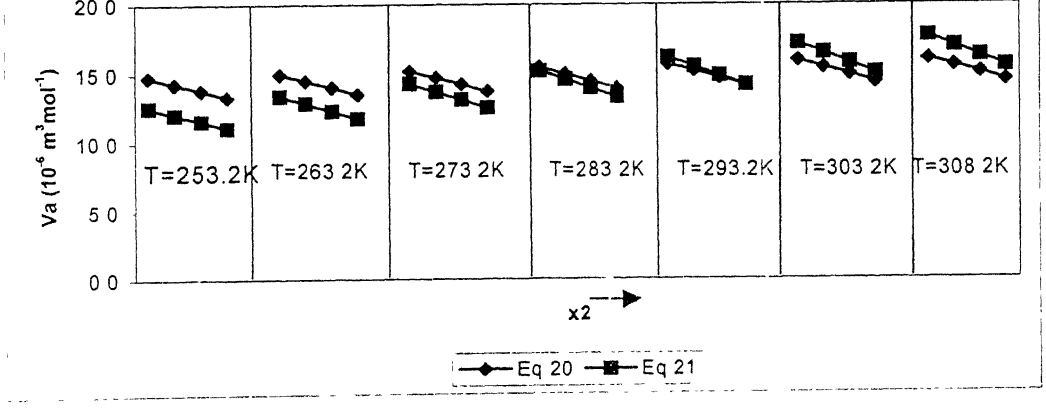
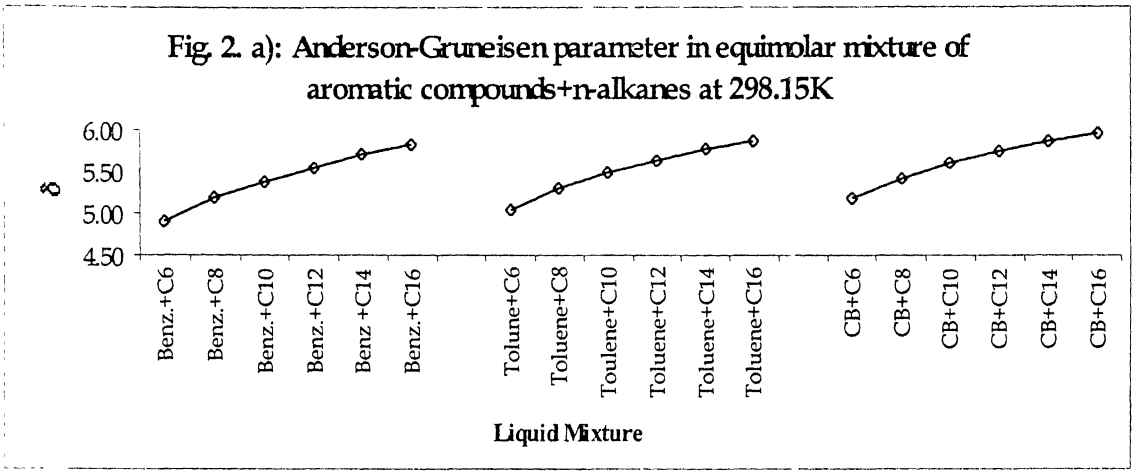
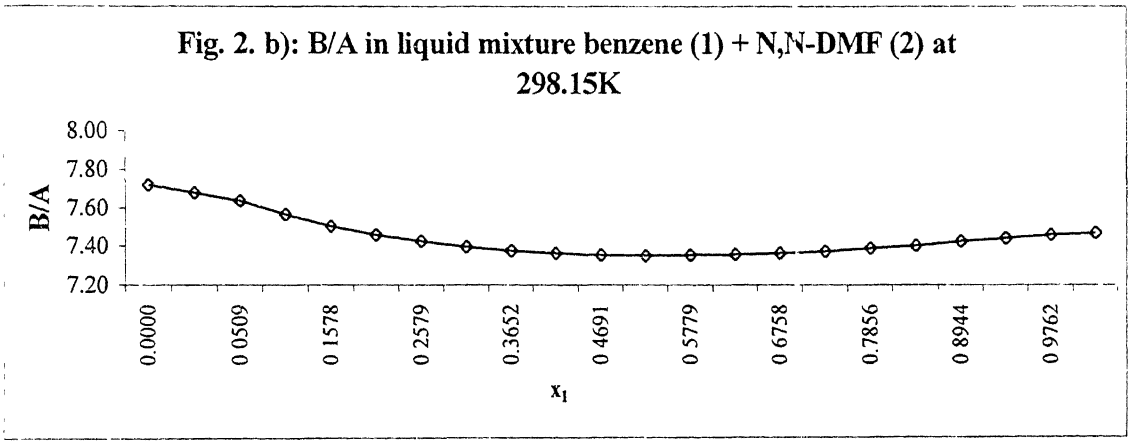
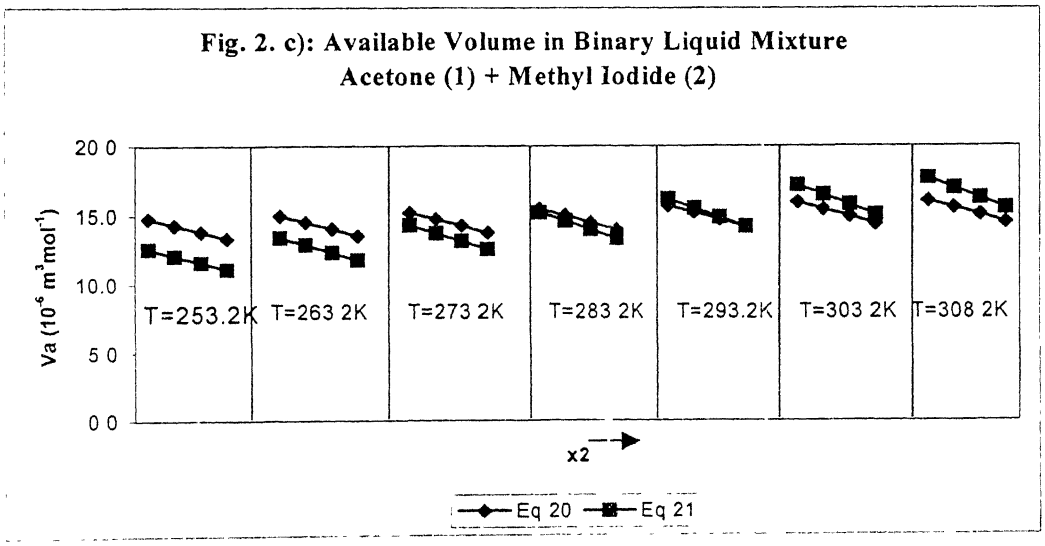


Fig. 2: Anderson-Gruneisen parameter, non-linear parameter and volumetric properties in binary liquid mixtures







CHAPTER – 8

Evaluation of viscosity of liquids and liquid mixtures

CHAPTER – 8

Evaluation of viscosity of liquids and liquid mixtures

8.1 Introduction

Viscosity is one of the important properties of the liquids and liquid mixtures, which is greatly used to study product designing and optimisation in chemical industries. Viscosity can be considered as a measure of internal fluid friction, which tends to oppose any dynamic change in the fluid motion. If the friction between the layers of fluids is small, i.e. viscosity of liquid is low, an applied shearing force will result in an increase in the velocity gradient. Similarly, there will be a decrease in the velocity gradient due to increase in the frictional drag on adjacent fluid layers. Owing such an important nature of viscosity, it has great number of relationships with various parameters of the liquid system.

Various theories of liquid system explain the relations for the evaluation of viscosity in various ways. Several approaches for the estimation of viscosity in liquids and liquid mixtures from other known parameters or viscosities of pure components of a liquid mixture are available. Methods of predicting viscosity of liquids and liquid mixtures based upon Free Volume Theory[1-5], Absolute Rate Theory[6], Statistical Thermodynamic Theory[7-8] and Significant Structure Theory[9-11], are some of the important approaches. Some concepts[12-17] to combine these different theories and simplify them in some valid ground are also useful for the prediction of viscosity with the help of minimum input data. Grunberg and Nissan[18] method (G-N) is another very important method for the prediction of viscosity of liquid mixtures. One constant G-N equation is convenient and reasonably accurate. This method utilises the interaction parameter (G_{ij}), which has been computed in various ways by various workers. Isdale et al[19] suggested group-contribution method to estimate the binary interaction parameter G_{ij}.

Wassiljewa[20] proposed a relation for the evaluation of transport property of gaseous mixtures. Wilke[21] proposed analogous relation for the prediction of viscosity of gaseous mixtures. Mason and Saxena[22] proposed a relation for the computation of the adjustable parameter, used in these equations. Besides these relations, many

empirical and semi empirical relations have been proposed[23-25] to evaluate the viscosity of liquid mixtures.

From literature survey, it has been found that several workers[26-48] have measured viscosity in liquids or utilised viscosity data to study molecular interactions or utilised the various relations to predict the viscosity of liquids and liquid mixtures. In most of these studies, viscosity of liquid mixtures are evaluated using empirical relations. Some attempts have been made to evaluate viscosity using Statistical model[29,33] and the model based upon Significant Structure theory[27,33]. The relation proposed by McAllister[25] has been extensively used by many workers[31,35,37,39-42]. In the present work, instead of all empirical relations, various categories of the relations for evaluation of viscosity of liquid mixtures have been used and tested in various mixtures of organic compounds. The Grunberg-Nissan method, which comprises the interaction parameter, has been used in conjunction with group contribution approach. As far as author's present knowledge is concerned, no detailed studies have been made in this approach, though the method was proposed earlier[19]. The model based upon the combination of Free Volume Theory, Absolute Rate Theory and Flory Statistical Theory has been given special emphasis. Besides these methods, the model based upon kinetic theory of gases proposed for the evaluation of transport properties of gaseous mixture[20,21], has also been utilized in liquid mixtures of organic compounds. For comparison with other models, only two simple empirical relations have been employed to evaluate viscosity of liquid mixtures.

Based upon the mole fraction additivity assumption in rheochor and molar volume, a new relation has been proposed here to compute the viscosity of liquid mixture from the knowledge of density and viscosity of the pure components. As far as author's present knowledge is concerned, same relation has not been purposed and used earlier. The relation has been tested for its validity in various liquid mixtures of organic compounds.

8.2 Theoretical

Some of the relations for the prediction for viscosity in the liquid mixtures have been discussed here.

(A) Relation based upon Absolute Rate Theory and Free Volume Theory in conjunction with Flory Statistical Theory

The Free Volume Theory assumes that there are probabilities of occurrence of empty neighboring sites in liquids, into which the molecules can jump[4,5]. The derivations of various relations in this assumption are based upon the following partition function of a molecule in a liquid [1,2]:

$$F_l = \frac{(2\pi mkT)^{3/2}}{h^3} V_f b_l e^{-E_0/RT} \qquad ...(1)$$

where, b_l is the combined vibrational and rotational contribution and E_o is the difference in energy per mole between the molecule in liquid and in the gas at 0 K, which may be approximated with enthalpy of vaporization (ΔE_{vap}). Other symbols have their usual meanings. The Absolute Rate Theory[6] relates viscosity to the free energy needed for a molecule to overcome the attractive force field of its neighbours, allowing molecule to jump in a new equilibrium position. Since probability of occurring empty neighbouring sites is related with the free volume of the liquid, it seems logical that these theories can be combined[12]. Based upon these concepts, Bloomfield and Dewan[14] examined the expression for the evaluation of viscosity of liquid mixtures. By the combination of the relations from these two theories, following expression can be derived for the evaluation of viscosity of liquid mixtures:

$$\eta = A.\exp\left\{(\Delta G^*/RT) + \gamma'(V^*/V_f)\right\} \qquad ...(2)$$

where, ΔG^* is the activation of free energy of viscous flow per mole, V^* is hard-core volume of a segment and V_f is the free energy per segment. The factor γ' is of the order of unity. For pure components of a liquid mixture, the above equation can be written as:

8.2 Theoretical

Some of the relations for the prediction for viscosity in the liquid mixtures have been discussed here.

(A) Relation based upon Absolute Rate Theory and Free Volume Theory in conjunction with Flory Statistical Theory

The Free Volume Theory assumes that there are probabilities of occurrence of empty neighboring sites in liquids, into which the molecules can jump[4,5]. The derivations of various relations in this assumption are based upon the following partition function of a molecule in a liquid [1,2]:

$$F_l = \frac{(2\pi mkT)^{3/2}}{h^3} V_f b_l e^{-E_0/RT} \qquad ...(1)$$

where, b_l is the combined vibrational and rotational contribution and E_o is the difference in energy per mole between the molecule in liquid and in the gas at 0 K, which may be approximated with enthalpy of vaporization (ΔE_{vap}). Other symbols have their usual meanings. The Absolute Rate Theory[6] relates viscosity to the free energy needed for a molecule to overcome the attractive force field of its neighbours, allowing molecule to jump in a new equilibrium position. Since probability of occurring empty neighbouring sites is related with the free volume of the liquid, it seems logical that these theories can be combined[12]. Based upon these concepts, Bloomfield and Dewan[14] examined the expression for the evaluation of viscosity of liquid mixtures. By the combination of the relations from these two theories, following expression can be derived for the evaluation of viscosity of liquid mixtures:

$$\eta = A.\exp\left\{(\Delta G^* / RT) + \gamma'(V^* / V_f)\right\} \qquad ...(2)$$

where, ΔG^* is the activation of free energy of viscous flow per mole, V^* is hard-core volume of a segment and V_f is the free energy per segment. The factor γ' is of the order of unity. For pure components of a liquid mixture, the above equation can be written as:

$$\eta = A.\exp\left\{(\Delta G_i^* / RT) + \gamma'(V_i^* / V_{f,i})\right\} \quad ...(3)$$

Using the assumption of Roseveare et al[13] ,

$$\Delta G^* = \left(\sum xi\Delta G_i^*\right) - \left(\alpha' \Delta G^R\right) \quad ...(4)$$

where, ΔG^R is residual free energy and is related to excess free energy of mixing. α' is a constant with an order of unity. ΔG^R is given as:

$$\Delta G^R = \Delta H_M - T\Delta S^R \quad ...(5)$$

where, ΔH_M is enthalpy of mixing per mole and ΔS^R is the residual entropy per mole. Reduced volume ($\widetilde{V}$) is given by the equation

$$\widetilde{V} = V / V^* \quad ...(6)$$

Using eqs (2) to (6) and some adjustments, the following relation can be obtained to evaluate the viscosity of liquid mixtures:

$$\ln \eta = \left(\sum x_i \ln \eta_i\right) - \left(\Delta H_M / RT\right) + \left(\Delta S^R / R\right) + \left[\frac{1}{\widetilde{V} - 1} - \sum \frac{x_i}{\widetilde{V}_i - 1}\right] \quad ...(7)$$

The four terms in eq (7) represent four different contributions, which are ideal mixture viscosity (η_{id}), enthalpy (η_H), residual entropy (η_s) and difference in the free volume between mixture and pure components (η_v). The above equation can be simply expressed in terms of various contributing terms as:

$$\ln \eta = \ln \eta_{id} + \ln \eta_H + \ln \eta_S + \ln \eta_v \quad ...(8)$$

where, contributing terms of eq (8) can be written as.

$$\eta_{id} = \exp\left[\sum x_i \ln \eta_i\right]$$

$$\eta_H = \exp\left[-\frac{\Delta H_M}{R}\right]$$

$$\eta_S = \exp\left[\frac{\Delta S^R}{R}\right]$$

$$\eta_v = \exp\left[\frac{1}{\tilde{V}-1} - \left(\sum \frac{x_i}{\tilde{V}_i - 1}\right)\right]$$

The residual frequency (ΔS^R) and enthalpy of mixing ΔH_M can be computed using the Flory relation[7,8]:

$$\Delta S^R = \sum\left\{-\frac{3x_i P_i^* V_i^*}{T_i^*} \ln\left(\frac{\tilde{V}_i^{1/3} - 1}{\tilde{V}^{1/3} - 1}\right)\right\} \qquad (9)$$

For binary liquid mixture,

$$\Delta H_M = x_1 P_1^* V_1^*\left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}}\right] + x_2 P_2^* V_2^*\left[\frac{1}{\tilde{V}_2} - \frac{1}{\tilde{V}}\right] + \frac{X_1 V_1^* \theta_2 X_{12}}{\tilde{V}_1} \qquad (10)$$

For ternary liquid mixture,

$$\Delta H_M = x_1 P_1^* V_1^*\left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}}\right] + x_2 P_2^* V_2^*\left[\frac{1}{\tilde{V}_2} - \frac{1}{\tilde{V}}\right] + x_3 P_3^* V_3^*\left[\frac{1}{\tilde{V}_3} - \frac{1}{\tilde{V}}\right] + \frac{x_1 V_1^* \theta_2 X_{12}}{\tilde{V}_1} + \frac{x_2 V_2^* \theta_3 X_{23}}{\tilde{V}_2} + \frac{x_3 V_3^* \theta_1 X_{31}}{\tilde{V}_3} \qquad (11)$$

The details about evaluation of the parameters like P_i^*, V_i^*, T_i^*, $\tilde{V}_i$, $\tilde{V}$ and X_{ij} have been given in chapter-3 of this thesis.

(B) Grunberg and Nissan Method in conjunction with Group Contribution Method

Grunberg and Nissan[18] proposed a comprehensive relation for the evaluation of viscosity in liquid mixture. Single parameter Grunberg-Nissan equation for binary liquid mixture can be expressed as:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \qquad ...(12)$$

where, G_{12} is an interaction parameter, which is a function of temperature and even composition. This relation has been utilised by some workers[26,36,38]. There are no

direct and convenient relations available for the evaluation of interaction parameter G_{ij}. In present study Group Contribution method proposed by Isdale et al[19] has been utilized to compute G_{ij}. The calculation of G_{ij} based upon this method uses the relation

$$G_{ij} = \sum \Delta_i + \sum \Delta_j + W \qquad ...(13)$$

where, W is a parameter evaluated using the relation

$$W = \frac{(0.3161)(N_i - N_j)^2}{(N_i + N_j)} - 0.1188(N_i - N_j) \qquad ...(14)$$

The parameters Δ_i, Δ_j, N_i and N_j for this particular method have to be computed using the contribution of groups on these parameters.

(C) Wassiljewa Method

Wassiljewa[20] proposed a relation for the evaluation of viscosity of liquid mixtures. Wilke[21] proposed analogous method, for the evaluation of viscosity of gaseous mixture. The relation in simplified form can be written as

$$\eta = \sum_i \frac{x_i \eta_i}{\sum_{j \neq i} A_{ij} x_j} \qquad ...(15)$$

where x_i is the mole fraction of i^{th} component and A_{ij} is the adjustable parameter. Simplified Mason and Saxena[21] relation for the evaluation of A_{ij} can be written as

$$A_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j}\right)^{-1/2} \left[1 + \left(\frac{\eta_i}{\eta_j}\right)^{1/2} \left(\frac{M_j}{M_i}\right)^{1/4}\right]^2 \qquad ...(16)$$

Owing some structural similarities of gases and liquids, the Wassiljewa relation is expected to be useful for the evaluation of viscosity of liquid mixture also.

(C) Bingham and Kendall –Munroe Methods

There are several empirical and semi-empirical relations proposed for the evaluation of viscosity of liquid mixtures. Most of these methods are interpolative. Only two relations out of them are discussed here for the comparison purpose. Bingham[24], based upon strict mole fraction additivity assumption in viscosity, proposed an empirical relation. The relation can be expressed as:

$$\eta = \sum x_i \eta_i \qquad \ldots(17)$$

Kendall-Munroe method for the computation of viscosity of liquid mixtures can be expressed as:

$$\ln \eta = \sum x_i \ln \eta_i \qquad \ldots(18)$$

(D) New Approach

Based upon the mole fraction additivity assumption of rheochor ([R]), which is given by

$$[R] = V\eta^{1/8} \qquad \ldots(19)$$

and the mole fraction additivity assumption in molar volume of liquid mixtures, the following relation has been proposed, which may be used for the evaluation of viscosity of the liquid mixtures:

$$\eta = \left[\frac{\sum\left(x_i V_i \eta_i^{1/8}\right)}{\sum\left(x_i V_i\right)}\right]^8 \qquad \ldots(20)$$

where, η is the viscosity of liquid mixture, x_i is the mole fraction of the components of the mixtures and V_i is the molar volumes of the components. As far as author's present knowledge is concerned, no such relation has been proposed and utilized. So this relation can be considered as a new approach for the computation of viscosity in liquid mixtures. One limitation of the above mentioned relation is that, it does not include the interaction parameter,

8.3 Results and Discussion

Six binary and two ternary liquid mixtures comprising various organic compounds have been considered under investigation. The eqs (7), (12), (15), (17), (18) and (20) were utilized to compute the viscosity of the liquid mixtures. The computed values were compared against the experimental values. The experimental values, computed values and percentage deviations in computed values for the same, have been depicted in tables-2 and 3. Table-1 lists some of the parameters of pure liquid components and interaction parameters of binary and ternary liquid mixtures. The necessary data for the computation of viscosity have been taken from literature[33,34,37,43]. The values of thermal expansion coefficient and isothermal compressibility, which are required for the computation of viscosity using a relation based upon Flory theory have also been taken from the literature[33,43].

Careful perusal of tables-2 and 3 reflect that, the method based upon Flory Statistical Theory (FST) gives satisfactory results in nearly all the systems under investigation. In most of the system under study, except in ternary liquid mixture of 1-chloronaphthalene + dodecane, the percentage deviations are low. The reason for this good agreement may be that, Flory theory clearly uses the interaction parameter, X_{ij}, in its relation, which is an important aspect of this theory. In 1-chloronaphthalene + dodecane system even, where all other relations give large deviations, this relation predicts the liquid mixture viscosity with an average percentage deviation of about 4. Wassiljewa relation (Wassil), though was proposed for estimating transport properties of gaseous mixtures, is surprisingly found to be quite applicable in the evaluation of the viscosity of the organic liquid mixtures of concern. The results from the relation are encouraging except in the case of 1-chloronaphthalene + dodecane. The large difference in the viscosities of the pure components, in this case, might be the reason for these deviations. Grunberg-Nissan method in conjunction with Group Contribution approach is also found to give very good results in most of the cases like carbon-tetrachloride + cyclohexane & n-heptane + n-hexane. In the case of 1-

8.3 Results and Discussion

Six binary and two ternary liquid mixtures comprising various organic compounds have been considered under investigation. The eqs (7), (12), (15), (17), (18) and (20) were utilized to compute the viscosity of the liquid mixtures. The computed values were compared against the experimental values. The experimental values, computed values and percentage deviations in computed values for the same, have been depicted in tables-2 and 3. Table-1 lists some of the parameters of pure liquid components and interaction parameters of binary and ternary liquid mixtures. The necessary data for the computation of viscosity have been taken from literature[33,34,37,43]. The values of thermal expansion coefficient and isothermal compressibility, which are required for the computation of viscosity using a relation based upon Flory theory have also been taken from the literature[33,43].

Careful perusal of tables-2 and 3 reflect that, the method based upon Flory Statistical Theory (FST) gives satisfactory results in nearly all the systems under investigation. In most of the system under study, except in ternary liquid mixture of 1-chloronaphthalene + dodecane, the percentage deviations are low. The reason for this good agreement may be that, Flory theory clearly uses the interaction parameter, X_{ij}, in its relation, which is an important aspect of this theory. In 1-chloronaphthalene + dodecane system even, where all other relations give large deviations, this relation predicts the liquid mixture viscosity with an average percentage deviation of about 4. Wassiljewa relation (Wassil), though was proposed for estimating transport properties of gaseous mixtures, is surprisingly found to be quite applicable in the evaluation of the viscosity of the organic liquid mixtures of concern. The results from the relation are encouraging except in the case of 1-chloronaphthalene + dodecane. The large difference in the viscosities of the pure components, in this case, might be the reason for these deviations. Grunberg-Nissan method in conjunction with Group Contribution approach is also found to give very good results in most of the cases like carbon-tetrachloride + cyclohexane & n-heptane + n-hexane. In the case of 1-

chloronaphthalene + dodecane, the large percentage differences ar
this method. These results indicate that aromatic compounds having
should be treated in a different way, while considering the con
aromatic ring, in the determination of the parameters like Δ_i and Δ_j.
like considering the contribution of one naphthalene ring as the con
benzene rings, should not be practiced. Bingham (Bingh) and Kenda
M) relations are found to give satisfactory results in the cases, where
the mixture have much similarity especially in terms of their viscositi
explanation for the applicability of these relations in the above-mentio
is that these relations are based upon strict mole fraction additivity a
viscosity.

Newly proposed method is found to give the satisfactory results in many
heptane + n-hexane, carbon-tetrachloride + cyclohexane, carbon-tetr
benzene, cyclohexane + benzene, 1- heptanol + 1-octanol and toluene + 1
hexane. Though larger deviations are observed in the case of 1-chlorona
dodecane, the deviations are less than in many other methods. The poss
for some deviations might be that, no interaction parameter has been int
the relation. This is one limitation of the present approach. Despite this lim
newly proposed relation may be considered as a convenient and reasonabl
method for the evaluation of viscosity of liquid mixture.

8.4 References

1. Eyring H & Hirschfelder J O, *J Phys Chem,* **41** (1937) 249.
2. Hirschfelder J O, *J Chem Edu,* **16** (1939) 540.
3. Bosworth R C L, *Trans Farad Soc,* **43** (1947) 308.
4. Williams M L, Landel R F & Ferry J D, *J Chem Soc,* 77 (1955) 3701.
5. Cohen M H, Turnbull D, *J Chem Phys,* **31** (1959) 1164.
6. Glasstone S, Laidler K J & Eyring H, *The Theory of Rate Process*

7. Flory P J, *J Am Chem Soc*, **87** (1965) 1833.
8. Flory P J, Orwoll R A, Vrij A, *J Am Chem Soc*, **86** (1964) 3507.
9. Eyring H, Ree T & Hirai H, *Proc Nat. Acad Sci USA*, **44** (1958) 683.
10. Eyring H & John M K, *Significant Liquid Structures*, Wiley, New York, 1969.
11. Eyring H & Ree T, *ibid*, **47** (1961) 526.
12. Macedo P B & Litovitz T A, *J Chem Phys*, **42** (1965) 245.
13. Roseveara W E, Powell R E & Eyring H, *J Appl Phys*, **12** (1941) 669.
14. Bloomfield V A, & Dewan R K, *J Phys Chem*, **75** (1971) 3113.
15. Schrodt J T, Arkel R M, J Chem Eng Data, **34** (1989) 8.
16. Frenkel J, Kinetic Theory of Gases, Oxford Univ Press, 1946.
17. Chapman S & Cowling T G, *The Mathematical Theory of Non-uniform Gases*, Cambridge press, Cambridge, 1939.
18. Grunberg L & Nissan A H, *Nature*, **164** (1949) 799.
19. Isdale J D, MacGillivray J C & Cartwright G, *Natl Eng Lab Rept*, Glasgaw, Scotland, 1985.
20. Wassiljewa A, *Phys*, **5** (1904) 737.
21. Wilke C R, *J Chem Phys*, **18** (1917) 1787.
22. Mason E A & Saxena S C, *Phys Fluids*, **1** (1958) 631.
23. Kendall J & Munroe K P, *J Am Chem Soc*, **39** (1917) 1787.
24. Bingham E C, *Fluidity and Plasticity*, McGrawHill, New York, 1992.
25. McAllister R A, *AIChE J*, **6** (1960) 427.
26. Chaturvedi B R & Pandey J D, *Chemica Scripta*, **15** (1980) 172.
27. Pandey J D & Gupta U, *Electrochim Acta*, **29(3)** (1984) 403.
28. Wu D T, *Fluid Phase Equilibria*, **30** (1986) 149.
29. Islam M R & Quadri S K, *Acoustics Letters*, **11(2)** (1988) 237.
30. Pandey J D, Agrawal N, Shikha & Mishra K, *Ind J Chem*, **29A** (1990) 113.
31. Acevedo I L & Kartz M, *J Soln Chem*, **10(19)** (1990) 1041.
32. Nath J & Choudhry S K, *J Chem Eng Data*, **37** (1992) 387.
33. Pandey J D, Pandey S, Gupta S & Shukla A K, *J Soln Chem*, **23(9)** (1994) 1049.
34. Pandey J D, Jain P & Vyas V, *J Soln Chem*, **72** (1994) 000.

35. Pal A & Kumar A, *Fluid Phase Equilibria,* **143** (1998) 241.
36. Oswal S L & Desai H S, *Fluid Phase Equilibria*, **149** (1998) 359.
37. Shan Z & Asfour A A, *Fluid Phase Equilibria,* **143** (1998) 253.
38. Dominguez M, Pardo J I, Gascon I, Royo F M, Urieta J S, *Fluid Phase Equilibria,* **169** (2000) 277.
39. Martinez S, Garriga R, Perez P & Gracia M, *Fluid Phase Equilibria,* **168** (2000) 267.
40. Gomez - Diaz D, Mejuto J C & Navaza J M, *J Chem Eng Data,* **46** (2001) 720.
41. Tu C, Lee S & Peng I, *J Chem Eng Data,* **46** (2001) 151.
42. Franjo C, Segade L, Menaut C P, Pico J M & Jimenez E, *J Soln Chem,* **30(11)** (2001) 996.
43. Aminabhavi T M & Banerjee K, *Ind J Chem,* **40A** (2001) 53.
44. Nayak J N, Aralaguppi M I & Aminabhavi T M, *J Chem Eng Data*, **47(4)** (2001) 964.
45. Cruz R C, Martins R J, Cardoso M J, Barcia O E, *J Chem Eng Data,* **47(4)** (2002) 927.
46. Victor P J & Hazra D K, *J Chem Eng Data*, **47** (2002) 79.
47. Manfredini M, Marchetti A, Sighinolfi S, Tessi L, Ulrici A, Vignoli M & Zucchi C, *J Soln Chem,* **31(3)** (2002) 235.
48. Marigliano A C, Solimo H N, *J Chem Eng Data,* **47(4)** (2002) 796.

Table –1

Various Parameters of binary and ternary liquid mixtures

Liquid Mixture	T (K)	$\eta_1/10^{-3}$ N s m^{-2}	$\eta_2/10^{-3}$ N s m^{-2}	$\eta_3/10^{-3}$ N s m^{-2}	$V_1/10^{-6}$ m^3mol^{-1}	$V_2/10^{-6}$ m^3mol^{-1}	$V_3/10^{-6}$ m^3mol^{-1}	G_{12}	A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}
ı) n-Heptane + n-hexane	298.15	0.3860	0.2940	-	147.50	131.57	-	0.002	1.064	0.942	-	-	-	-
›) CCl_4 + cyclohexane	298.15	0.9004	0.8950	-	97.08	108.76	-	-0.026	0.729	1.325	-	-	-	-
;) CCl_4 + benzene	298.15	0.9004	0.6036	-	97.08	89.41	-	0.324	0.846	1.117	-	-	-	-
l) Cyclohexane + benzene	298.15	0.8950	0.6036	-	108.76	89.41	-	-0.350	1.182	0.859	-	-	-	-
) Chloronaphthalene + dodecane	298.15	3.0750	1.2460	-	136.90	228.20	-	-1.438	1.695	0.656	-	-	-	-
) 1-Heptanol + 1-octanol	308.15	4.3250	5.4580	-	143.16	159.81	-	0.129	0.943	1.062	-	-	-	-
	313.15	3.7210	4.6460	-	143.76	160.48	-	0.146	0.948	1.056	-	-	-	-
) 1-Pentanol + 1-octanol	308.15	2.6520	5.4580	-	109.69	159.81	-	0.314	0.854	1.190	-	-	-	-
	313.15	2.3330	4.6460	-	110.20	160.48	-	0.327	0.866	1.168	-	-	-	-
) Toluene + n-heptane + n-hexane	298.15	0.6036	0.3860	0.2940	106.88	147.50	131.57	-	1.323	0.778	1.426	0.743	1.064	0.942
CCl_4 + cyclohexane + benzene	298.15	0.9004	0.8950	0.6036	97.08	108.76	89.41	-	0.729	1.325	0.846	1.117	1.182	0.859

Table –2

Experimental and Computed values of viscosity (η) in binary liquid mixtures

2. a) Binary liquid mixture: n- heptane + n- hexane

x_1	x_2	T	$\eta/10^{-3}$	FST		Wassil		Grp Contr		Bingh		K-M		New Approach	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	0.2940	0.2940	0.00	0.2940	0.00	0.2940	0.00	0.2940	0.00	0.2940	0.00	0.2940	0.00
0.2069	0.7931	298.15	0.3145	0.3120	0.80	0.3120	0.79	0.3111	1.08	0.3130	0.47	0.3110	1.10	0.3129	0.50
0.2351	0.7649	298.15	0.3160	0.3145	0.48	0.3145	0.47	0.3135	0.79	0.3156	0.12	0.3134	0.81	0.3155	0.15
0.2637	0.7363	298.15	0.3170	0.3170	-0.01	0.3171	-0.02	0.3160	0.32	0.3183	-0.40	0.3159	0.35	0.3182	-0.36
0.2929	0.7071	298.15	0.3190	0.3196	-0.20	0.3197	-0.21	0.3185	0.16	0.3209	-0.61	0.3184	0.19	0.3208	-0.58
0.3129	0.6871	298.15	0.3200	0.3214	-0.44	0.3215	-0.45	0.3202	-0.08	0.3228	-0.87	0.3201	-0.04	0.3227	-0.84
0.3665	0.6335	298.15	0.3245	0.3262	-0.54	0.3263	-0.55	0.3250	-0.14	0.3277	-0.99	0.3248	-0.11	0.3276	-0.96
0.3904	0.6096	298.15	0.3250	0.3284	-1.05	0.3284	-1.06	0.3271	-0.64	0.3299	-1.51	0.3270	-0.61	0.3298	-1.48
0.4267	0.5733	298.15	0.3275	0.3317	-1.28	0.3317	-1.29	0.3303	-0.87	0.3333	-1.76	0.3302	-0.83	0.3331	-1.72
0.4687	0.5313	298.15	0.3310	0.3355	-1.37	0.3356	-1.38	0.3341	-0.95	0.3371	-1.85	0.3340	-0.91	0.3370	-1.82
0.5072	0.4928	298.15	0.3345	0.3391	-1.37	0.3391	-1.37	0.3377	-0.95	0.3407	-1.84	0.3375	-0.91	0.3406	-1.81
0.5526	0.4474	298.15	0.3380	0.3433	-1.56	0.3433	-1.56	0.3419	-1.14	0.3448	-2.02	0.3417	-1.10	0.3447	-1.99
0.5994	0.4006	298.15	0.3440	0.3476	-1.05	0.3476	-1.05	0.3462	-0.65	0.3491	-1.50	0.3461	-0.61	0.3491	-1.47
0.6507	0.3493	298.15	0.3500	0.3524	-0.69	0.3524	-0.69	0.3511	-0.32	0.3539	-1.10	0.3510	-0.28	0.3538	-1.08
0.6881	0.3119	298.15	0.3550	0.3559	-0.27	0.3559	-0.27	0.3547	0.09	0.3573	-0.65	0.3546	0.12	0.3572	-0.63
0.7280	0.2720	298.15	0.3600	0.3597	0.08	0.3597	0.08	0.3586	0.40	0.3610	-0.27	0.3584	0.43	0.3609	-0.25
1.0000	0.0000	298.15	0.3860	0.3860	0.00	0.3860	0.00	0.3860	0.00	0.3860	0.00	0.3860	0.00	0.3860	0.00
		APD:			**-0.50**		**-0.50**		**-0.17**		**-0.87**		**-0.14**		**-0.84**

Table –2

Experimental and Computed values of viscosity (η) in binary liquid mixtures

2. a) Binary liquid mixture: n- heptane + n- hexane

x_1	x_2	T	$\eta/10^{-3}$	FST		Wassil		Grp Contr		Bingh		K-M		New Approach	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	0.2940	0.2940	0.00	0.2940	0.00	0.2940	0.00	0.2940	0.00	0.2940	0.00	0.2940	0.00
0.2069	0.7931	298.15	0.3145	0.3120	0.80	0.3120	0.79	0.3111	1.08	0.3130	0.47	0.3110	1.10	0.3129	0.50
0.2351	0.7649	298.15	0.3160	0.3145	0.48	0.3145	0.47	0.3135	0.79	0.3156	0.12	0.3134	0.81	0.3155	0.15
0.2637	0.7363	298.15	0.3170	0.3170	-0.01	0.3171	-0.02	0.3160	0.32	0.3183	-0.40	0.3159	0.35	0.3182	-0.36
0.2929	0.7071	298.15	0.3190	0.3196	-0.20	0.3197	-0.21	0.3185	0.16	0.3209	-0.61	0.3184	0.19	0.3208	-0.58
0.3129	0.6871	298.15	0.3200	0.3214	-0.44	0.3215	-0.45	0.3202	-0.08	0.3228	-0.87	0.3201	-0.04	0.3227	-0.84
0.3665	0.6335	298.15	0.3245	0.3262	-0.54	0.3263	-0.55	0.3250	-0.14	0.3277	-0.99	0.3248	-0.11	0.3276	-0.96
0.3904	0.6096	298.15	0.3250	0.3284	-1.05	0.3284	-1.06	0.3271	-0.64	0.3299	-1.51	0.3270	-0.61	0.3298	-1.48
0.4267	0.5733	298.15	0.3275	0.3317	-1.28	0.3317	-1.29	0.3303	-0.87	0.3333	-1.76	0.3302	-0.83	0.3331	-1.72
0.4687	0.5313	298.15	0.3310	0.3355	-1.37	0.3356	-1.38	0.3341	-0.95	0.3371	-1.85	0.3340	-0.91	0.3370	-1.82
0.5072	0.4928	298.15	0.3345	0.3391	-1.37	0.3391	-1.37	0.3377	-0.95	0.3407	-1.84	0.3375	-0.91	0.3406	-1.81
0.5526	0.4474	298.15	0.3380	0.3433	-1.56	0.3433	-1.56	0.3419	-1.14	0.3448	-2.02	0.3417	-1.10	0.3447	-1.99
0.5994	0.4006	298.15	0.3440	0.3476	-1.05	0.3476	-1.05	0.3462	-0.65	0.3491	-1.50	0.3461	-0.61	0.3491	-1.47
0.6507	0.3493	298.15	0.3500	0.3524	-0.69	0.3524	-0.69	0.3511	-0.32	0.3539	-1.10	0.3510	-0.28	0.3538	-1.08
0.6881	0.3119	298.15	0.3550	0.3559	-0.27	0.3559	-0.27	0.3547	0.09	0.3573	-0.65	0.3546	0.12	0.3572	-0.63
0.7280	0.2720	298.15	0.3600	0.3597	0.08	0.3597	0.08	0.3586	0.40	0.3610	-0.27	0.3584	0.43	0.3609	-0.25
1.0000	0.0000	298.15	0.3860	0.3860	0.00	0.3860	0.00	0.3860	0.00	0.3860	0.00	0.3860	0.00	0.3860	0.00
		APD:			**-0.50**		**-0.50**		**-0.17**		**-0.87**		**-0.14**		**-0.84**

Table –2

Experimental and Computed values of viscosity (η) in binary liquid mixtures

2. a) Binary liquid mixture: n- heptane + n- hexane

x_1	x_2	T	$\eta/10^{-3}$	FST		Wassil		Grp Contr		Bingh		K-M		New Approach	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	0.2940	0.2940	0.00	0.2940	0.00	0.2940	0.00	0.2940	0.00	0.2940	0.00	0.2940	0.00
0.2069	0.7931	298.15	0.3145	0.3120	0.80	0.3120	0.79	0.3111	1.08	0.3130	0.47	0.3110	1.10	0.3129	0.50
0.2351	0.7649	298.15	0.3160	0.3145	0.48	0.3145	0.47	0.3135	0.79	0.3156	0.12	0.3134	0.81	0.3155	0.15
0.2637	0.7363	298.15	0.3170	0.3170	-0.01	0.3171	-0.02	0.3160	0.32	0.3183	-0.40	0.3159	0.35	0.3182	-0.36
0.2929	0.7071	298.15	0.3190	0.3196	-0.20	0.3197	-0.21	0.3185	0.16	0.3209	-0.61	0.3184	0.19	0.3208	-0.58
0.3129	0.6871	298.15	0.3200	0.3214	-0.44	0.3215	-0.45	0.3202	-0.08	0.3228	-0.87	0.3201	-0.04	0.3227	-0.84
0.3665	0.6335	298.15	0.3245	0.3262	-0.54	0.3263	-0.55	0.3250	-0.14	0.3277	-0.99	0.3248	-0.11	0.3276	-0.96
0.3904	0.6096	298.15	0.3250	0.3284	-1.05	0.3284	-1.06	0.3271	-0.64	0.3299	-1.51	0.3270	-0.61	0.3298	-1.48
0.4267	0.5733	298.15	0.3275	0.3317	-1.28	0.3317	-1.29	0.3303	-0.87	0.3333	-1.76	0.3302	-0.83	0.3331	-1.72
0.4687	0.5313	298.15	0.3310	0.3355	-1.37	0.3356	-1.38	0.3341	-0.95	0.3371	-1.85	0.3340	-0.91	0.3370	-1.82
0.5072	0.4928	298.15	0.3345	0.3391	-1.37	0.3391	-1.37	0.3377	-0.95	0.3407	-1.84	0.3375	-0.91	0.3406	-1.81
0.5526	0.4474	298.15	0.3380	0.3433	-1.56	0.3433	-1.56	0.3419	-1.14	0.3448	-2.02	0.3417	-1.10	0.3447	-1.99
0.5994	0.4006	298.15	0.3440	0.3476	-1.05	0.3476	-1.05	0.3462	-0.65	0.3491	-1.50	0.3461	-0.61	0.3491	-1.47
0.6507	0.3493	298.15	0.3500	0.3524	-0.69	0.3524	-0.69	0.3511	-0.32	0.3539	-1.10	0.3510	-0.28	0.3538	-1.08
0.6881	0.3119	298.15	0.3550	0.3559	-0.27	0.3559	-0.27	0.3547	0.09	0.3573	-0.65	0.3546	0.12	0.3572	-0.63
0.7280	0.2720	298.15	0.3600	0.3597	0.08	0.3597	0.08	0.3586	0.40	0.3610	-0.27	0.3584	0.43	0.3609	-0.25
1.0000	0.0000	298.15	0.3860	0.3860	0.00	0.3860	0.00	0.3860	0.00	0.3860	0.00	0.3860	0.00	0.3860	0.00
		APD:			**-0.50**		**-0.50**		**-0.17**		**-0.87**		**-0.14**		**-0.84**

2. b) Binary liquid mixture: Carbon tetrachloride + cyclohexane

x_1	x_2	T	$\eta/ 10^{-3}$	FST		Wassil		Grp Contr		Bingh		K-M		New Approach	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	0.8950	0.8950	0.00	0.8950	0.00	0.8950	0.00	0.8950	0.00	0.8950	0.00	0.8950	0.00
0.2753	0.7247	298.15	0.8903	0.8963	-0.67	0.9036	-1.50	0.8918	-0.17	0.8965	-0.69	0.8965	-0.69	0.8964	-0.68
0.3845	0.6155	298.15	0.8916	0.8968	-0.59	0.9050	-1.50	0.8916	0.00	0.8971	-0.61	0.8971	-0.61	0.8969	-0.60
0.4418	0.5582	298.15	0.8929	0.8971	-0.48	0.9054	-1.40	0.8916	0.14	0.8974	-0.50	0.8974	-0.50	0.8972	-0.49
0.4727	0.5273	298.15	0.8928	0.8973	-0.50	0.9055	-1.42	0.8918	0.12	0.8976	-0.53	0.8975	-0.53	0.8974	-0.51
0.5800	0.4200	298.15	0.8943	0.8979	-0.40	0.9054	-1.24	0.8925	0.21	0.8981	-0.43	0.8981	-0.43	0.8980	-0.41
0.6707	0.3293	298.15	0.8955	0.8984	-0.32	0.9049	-1.05	0.8935	0.23	0.8986	-0.35	0.8986	-0.35	0.8985	-0.33
0.6805	0.3195	298.15	0.8956	0.8985	-0.32	0.9048	-1.03	0.8936	0.22	0.8987	-0.34	0.8987	-0.34	0.8985	-0.33
0.7701	0.2299	298.15	0.8969	0.8990	-0.23	0.9039	-0.78	0.8950	0.21	0.8992	-0.25	0.8992	-0.25	0.8990	-0.24
0.8640	0.1360	298.15	0.8982	0.8995	-0.15	0.9027	-0.50	0.8969	0.14	0.8997	-0.16	0.8997	-0.16	0.8996	-0.15
1.0000	0.0000	298.15	0.9004	0.9004	0.00	0.9004	0.00	0.9004	0.00	0.9004	0.00	0.9004	0.00	0.9004	0.00
		APD:			**-0.33**		**-0.95**		**0.10**		**-0.35**		**-0.35**		**-0.34**

2. c) Binary liquid mixture: Carbon tetrachloride + benzene

x_1	x_2	T	$\eta/ 10^{-3}$	FST		Wassil		Grp Contr		Bingh		K-M		New Approach	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	0.6036	0.6036	0.00	0.6036	0.00	0.6036	0.00	0.6036	0.00	0.6036	0.00	0.6036	0.00
0.1367	0.8633	298.15	0.6400	0.6368	0.51	0.6548	-2.31	0.6624	-3.49	0.6442	-0.65	0.6375	0.39	0.6409	-0.14
0.1809	0.8191	298.15	0.6530	0.6479	0.78	0.6705	-2.67	0.6808	-4.26	0.6573	-0.66	0.6489	0.63	0.6532	-0.03
0.2176	0.7824	298.15	0.6640	0.6574	1.00	0.6832	-2.89	0.6958	-4.79	0.6682	-0.63	0.6585	0.83	0.6635	0.08
0.2521	0.7479	298.15	0.6720	0.6664	0.84	0.6949	-3.41	0.7097	-5.61	0.6784	-0.96	0.6676	0.65	0.6732	-0.18
0.2882	0.7118	298.15	0.6800	0.6760	0.60	0.7069	-3.96	0.7239	-6.45	0.6891	-1.34	0.6773	0.39	0.6835	-0.51
0.3188	0.6812	298.15	0.6880	0.6842	0.55	0.7169	-4.21	0.7357	-6.93	0.6982	-1.49	0.6857	0.34	0.6922	-0.61
0.3463	0.6537	298.15	0.6970	0.6917	0.76	0.7258	-4.13	0.7460	-7.03	0.7064	-1.35	0.6933	0.54	0.7001	-0.45

0.4713	0.5287	298.15	0.7350	0.7270	1.09	0.7643	-3.98	0.7901	-7.49	0.7435	-1.15	0.7288	0.84	0.7366	-0.22
0.6150	0.3850	298.15	0.7750	0.7701	0.63	0.8053	-3.91	0.8335	-7.54	0.7861	-1.44	0.7719	0.40	0.7797	-0.60
1.0000	0.0000	298.15	0.9004	0.9004	0.00	0.9004	0.00	0.9004	0.00	0.9004	0.00	0.9004	0.00	0.9004	0.00
		APD:			**0.61**		**-2.86**		**-4.87**		**-0.88**		**0.46**		**-0.24**

2. d) Binary liquid mixture: Cyclohexane + benzene

x_1	x_2	T	$\eta/ 10^{-3}$	FST		Wassil		Grp Contr		Bingh		K-M		New Approach	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	0.6036	0.6036	0.00	0.6036	0.00	0.6036	0.00	0.6036	0.00	0.6036	0.00	0.6036	0.00
0.2942	0.7058	298.15	0.6780	0.6753	0.40	0.6778	0.03	0.6303	7.04	0.6893	-1.67	0.6778	0.03	0.6906	-1.86
0.2613	0.7387	298.15	0.6690	0.6668	0.34	0.6691	-0.01	0.6253	6.53	0.6797	-1.61	0.6690	-0.01	0.6809	-1.78
0.2368	0.7632	298.15	0.6650	0.6605	0.68	0.6627	0.35	0.6220	6.47	0.6726	-1.14	0.6626	0.36	0.6737	-1.31
0.1692	0.8308	298.15	0.6600	0.6436	2.49	0.6453	2.23	0.6142	6.94	0.6529	1.08	0.6452	2.24	0.6537	0.95
0.1659	0.8341	298.15	0.6570	0.6428	2.17	0.6444	1.91	0.6139	6.56	0.6519	0.77	0.6444	1.92	0.6527	0.65
0.1226	0.8774	298.15	0.6540	0.6322	3.33	0.6335	3.13	0.6101	6.72	0.6393	2.24	0.6335	3.14	0.6399	2.15
0.1770	0.8230	298.15	0.6540	0.6455	1.30	0.6473	1.03	0.6150	5.96	0.6552	-0.18	0.6472	1.04	0.6560	-0.31
0.2951	0.7049	298.15	0.6740	0.6755	-0.23	0.6780	-0.60	0.6304	6.47	0.6896	-2.31	0.6780	-0.59	0.6909	-2.51
0.6686	0.3314	298.15	0.7870	0.7826	0.56	0.7852	0.23	0.7269	7.64	0.7984	-1.45	0.7855	0.19	0.8001	-1.67
1.0000	0.0000	298.15	0.8950	0.8950	0.00	0.8950	0.00	0.8950	0.00	0.8950	0.00	0.8950	0.00	0.8950	0.00
		APD:			**1.00**		**0.75**		**5.48**		**-0.39**		**0.76**		**-0.52**

0.4713	0.5287	298.15	0.7350	0.7270	1.09	0.7643	-3.98	0.7901	-7.49	0.7435	-1.15	0.7288	0.84	0.7366	-0.22
0.6150	0.3850	298.15	0.7750	0.7701	0.63	0.8053	-3.91	0.8335	-7.54	0.7861	-1.44	0.7719	0.40	0.7797	-0.60
1.0000	0.0000	298.15	0.9004	0.9004	0.00	0.9004	0.00	0.9004	0.00	0.9004	0.00	0.9004	0.00	0.9004	0.00
		APD:			**0.61**		**-2.86**		**-4.87**		**-0.88**		**0.46**		**-0.24**

2. d) Binary liquid mixture: Cyclohexane + benzene

x_1	x_2	T	$\eta/ 10^{-3}$	FST		Wassil		Grp Contr		Bingh		K-M		New Approach	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	0.6036	0.6036	0.00	0.6036	0.00	0.6036	0.00	0.6036	0.00	0.6036	0.00	0.6036	0.00
0.2942	0.7058	298.15	0.6780	0.6753	0.40	0.6778	0.03	0.6303	7.04	0.6893	-1.67	0.6778	0.03	0.6906	-1.86
0.2613	0.7387	298.15	0.6690	0.6668	0.34	0.6691	-0.01	0.6253	6.53	0.6797	-1.61	0.6690	-0.01	0.6809	-1.78
0.2368	0.7632	298.15	0.6650	0.6605	0.68	0.6627	0.35	0.6220	6.47	0.6726	-1.14	0.6626	0.36	0.6737	-1.31
0.1692	0.8308	298.15	0.6600	0.6436	2.49	0.6453	2.23	0.6142	6.94	0.6529	1.08	0.6452	2.24	0.6537	0.95
0.1659	0.8341	298.15	0.6570	0.6428	2.17	0.6444	1.91	0.6139	6.56	0.6519	0.77	0.6444	1.92	0.6527	0.65
0.1226	0.8774	298.15	0.6540	0.6322	3.33	0.6335	3.13	0.6101	6.72	0.6393	2.24	0.6335	3.14	0.6399	2.15
0.1770	0.8230	298.15	0.6540	0.6455	1.30	0.6473	1.03	0.6150	5.96	0.6552	-0.18	0.6472	1.04	0.6560	-0.31
0.2951	0.7049	298.15	0.6740	0.6755	-0.23	0.6780	-0.60	0.6304	6.47	0.6896	-2.31	0.6780	-0.59	0.6909	-2.51
0.6686	0.3314	298.15	0.7870	0.7826	0.56	0.7852	0.23	0.7269	7.64	0.7984	-1.45	0.7855	0.19	0.8001	-1.67
1.0000	0.0000	298.15	0.8950	0.8950	0.00	0.8950	0.00	0.8950	0.00	0.8950	0.00	0.8950	0.00	0.8950	0.00
		APD:			**1.00**		**0.75**		**5.48**		**-0.39**		**0.76**		**-0.52**

2. e) Binary liquid mixture: Chloronaphthalene + dodecane

x_1	x_2	T	$\eta/ 10^{-3}$	FST		Wassil		Grp Contr		Bingh		K-M		New Approach	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	1.2460	1.2460	0.00	1.2460	0.00	1.2460	0.00	1.2460	0.00	1.2460	0.00	1.2460	0.00
0.0988	0.9012	298.15	1.3060	1.3154	-0.72	1.3492	-3.31	1.1986	8.22	1.4267	-9.24	1.3623	-4.31	1.3215	-1.18
0.1953	0.8047	298.15	1.3930	1.3947	-0.12	1.4600	-4.81	1.1857	14.88	1.6032	-15.09	1.4864	-6.71	1.4057	-0.92
0.2927	0.7073	298.15	1.4450	1.4885	-3.01	1.5834	-9.58	1.2052	16.59	1.7813	-23.28	1.6231	-12.33	1.5037	-4.06
0.3910	0.6090	298.15	1.5330	1.6005	-4.40	1.7215	-12.29	1.2595	17.84	1.9611	-27.93	1.7739	-15.71	1.6186	-5.58
0.4954	0.5046	298.15	1.6630	1.7430	-4.81	1.8857	-13.39	1.3607	18.18	2.1521	-29.41	1.9493	-17.22	1.7626	-5.99
0.5939	0.4061	298.15	1.7700	1.9054	-7.65	2.0601	-16.39	1.5063	14.90	2.3322	-31.77	2.1307	-20.38	1.9248	-8.75
0.6916	0.3084	298.15	1.9550	2.1007	-7.45	2.2555	-15.37	1.7126	12.40	2.5109	-28.44	2.3273	-19.04	2.1181	-8.34
0.8196	0.1804	298.15	2.2650	2.4249	-7.06	2.5525	-12.69	2.1122	6.75	2.7450	-21.19	2.6126	-15.35	2.4368	-7.58
0.8992	0.1008	298.15	2.5370	2.6780	-5.56	2.7658	-9.02	2.4643	2.87	2.8906	-13.94	2.8074	-10.66	2.6850	-5.83
1.0000	0.0000	298.15	3.0750	3.0750	0.00	3.0750	0.00	3.0750	0.00	3.0750	0.00	3.0750	0.00	3.0750	0.00
APD:					**-3.71**		**-8.80**		**10.24**		**-18.21**		**-11.06**		**-4.39**

2. f) Binary liquid mixture: 1- heptanol + 1-octanol

x_1	x_2	T	$\eta/ 10^{-3}$	Wassil		Grp Contr		Bingh		K-M		New Approach	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	308.15	5.4580	5.4580	0.00	5.4580	0.00	5.4580	0.00	5.4580	0.00	5.4580	0.00
0.1671	0.8329	308.15	5.2360	5.2575	-0.41	5.3452	-2.09	5.2687	-0.62	5.2499	-0.26	5.2702	-0.65
0.3071	0.6929	308.15	5.0840	5.0932	-0.18	5.2234	-2.74	5.1101	-0.51	5.0816	0.05	5.1123	-0.56
0.4819	0.5181	308.15	4.8850	4.8925	-0.15	5.0393	-3.16	4.9120	-0.55	4.8791	0.12	4.9144	-0.60
0.6319	0.3681	308.15	4.7130	4.7240	-0.23	4.8557	-3.03	4.7421	-0.62	4.7117	0.03	4.7441	-0.66
0.6868	0.3132	308.15	4.6460	4.6633	-0.37	4.7832	-2.95	4.6799	-0.73	4.6519	-0.13	4.6817	-0.77
0.8784	0.1216	308.15	4.4360	4.4546	-0.42	4.5110	-1.69	4.4628	-0.60	4.4491	-0.30	4.4636	-0.62
1.0000	0.0000	308.15	4.3250	4.3250	0.00	4.3250	0.00	4.3250	0.00	4.3250	0.00	4.3250	0.00
0.0000	1.0000	313.15	4.6460	4.6460	0.00	4.6460	0.00	4.6460	0.00	4.6460	0.00	4.6460	0.00
0.1671	0.8329	313.15	4.4750	4.4833	-0.18	4.5686	-2.09	4.4914	-0.37	4.4768	-0.04	4.4933	-0.41
0.3071	0.6929	313.15	4.3420	4.3496	-0.17	4.4765	-3.10	4.3619	-0.46	4.3398	0.05	4.3646	-0.52
0.4819	0.5181	313.15	4.1660	4.1859	-0.48	4.3294	-3.92	4.2002	-0.82	4.1746	-0.21	4.2033	-0.89
0.6319	0.3681	313.15	4.0490	4.0482	0.02	4.1772	-3.17	4.0615	-0.31	4.0379	0.28	4.0642	-0.37
0.6868	0.3132	313.15	3.9830	3.9985	-0.39	4.1160	-3.34	4.0107	-0.70	3.9889	-0.15	4.0132	-0.76
0.8784	0.1216	313.15	3.8080	3.8275	-0.51	3.8828	-1.96	3.8335	-0.67	3.8228	-0.39	3.8346	-0.70
1.0000	0.0000	313.15	3.7210	3.7210	0.00	3.7210	0.00	3.7210	0.00	3.7210	0.00	3.7210	0.00
		APD:			**-0.22**		**-2.08**		**-0.43**		**-0.06**		**-0.47**

2. g) Binary liquid mixture: 1- Pentanol + 1-octanol

x_1	x_2	T	$\eta/ 10^{-3}$	Wassil		Grp Contr		Bingh		K-M		New Approach	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	308.15	5.4580	5.4580	0.00	5.4580	0.00	5.4580	0.00	5.4580	0.00	5.4580	0.00
0.0849	0.9151	308.15	5.1400	5.1754	-0.69	5.2605	-2.34	5.2198	-1.55	5.1336	0.12	5.2365	-1.88
0.2664	0.7336	308.15	4.5890	4.6028	-0.30	4.7885	-4.35	4.7105	-2.65	4.5033	1.87	4.7502	-3.51
0.3696	0.6304	308.15	4.2800	4.2951	-0.35	4.4976	-5.08	4.4209	-3.29	4.1800	2.34	4.4662	-4.35
0.6046	0.3954	308.15	3.6370	3.6379	-0.02	3.8032	-4.57	3.7615	-3.42	3.5279	3.00	3.8023	-4.55
0.7080	0.2920	308.15	3.3560	3.3664	-0.31	3.4940	-4.11	3.4714	-3.44	3.2742	2.44	3.5040	-4.41
0.8575	0.1425	308.15	2.9840	2.9915	-0.25	3.0544	-2.36	3.0519	-2.27	2.9393	1.50	3.0685	-2.83
1.0000	0.0000	308.15	2.6520	2.6520	0.00	2.6520	0.00	2.6520	0.00	2.6520	0.00	2.6520	0.00
0.0000	1.0000	313.15	4.6460	4.6460	0.00	4.6460	0.00	4.6460	0.00	4.6460	0.00	4.6460	0.00
0.0849	0.9151	313.15	4.3820	4.4176	-0.81	4.4949	-2.58	4.4496	-1.54	4.3821	0.00	4.4655	-1.91
0.2664	0.7336	313.15	3.9390	3.9517	-0.32	4.1224	-4.66	4.0298	-2.31	3.8671	1.83	4.0681	-3.28
0.3696	0.6304	313.15	3.7020	3.6996	0.07	3.8870	-5.00	3.7911	-2.41	3.6017	2.71	3.8354	-3.60
0.6046	0.3954	313.15	3.1510	3.1572	-0.20	3.3127	-5.13	3.2476	-3.06	3.0634	2.78	3.2890	-4.38
0.7080	0.2920	313.15	2.9290	2.9315	-0.09	3.0525	-4.22	3.0084	-2.71	2.8528	2.60	3.0424	-3.87
0.8575	0.1425	313.15	2.6130	2.6182	-0.20	2.6786	-2.51	2.6626	-1.90	2.5736	1.51	2.6808	-2.59
1.0000	0.0000	313.15	2.3330	2.3330	0.00	2.3330	0.00	2.3330	0.00	2.3330	0.00	2.3330	0.00
APD:					**-0.22**		**-2.93**		**-1.91**		**1.42**		**-2.57**

Table –3

Experimental and Computed values of viscosity in ternary liquid mixtures

3. a) Ternary liquid mixture: Toluene + heptane + hexane

x_1	x_2	x_3	T	$\eta/10^{-3}$	FST		Wassil		Bingh		K-M		New Approach	
			(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.
0.1210	0.1838	0.6952	298.15	0.3354	0.3356	-0.06	0.3369	-0.45	0.3484	-3.87	0.3372	-0.54	0.3348	0.17
0.1459	0.2011	0.6530	298.15	0.3405	0.3429	-0.69	0.3444	-1.14	0.3577	-5.04	0.3449	-1.29	0.3418	-0.38
0.1698	0.2170	0.6132	298.15	0.3458	0.3499	-1.19	0.3516	-1.69	0.3665	-6.00	0.3524	-1.91	0.3486	-0.81
0.1929	0.2358	0.5713	298.15	0.3528	0.3572	-1.25	0.3591	-1.80	0.3754	-6.41	0.3602	-2.09	0.3556	-0.81
0.2160	0.2544	0.5296	298.15	0.3589	0.3647	-1.61	0.3668	-2.19	0.3843	-7.07	0.3680	-2.55	0.3628	-1.09
0.2390	0.2726	0.4884	298.15	0.3656	0.3722	-1.81	0.3745	-2.43	0.3931	-7.51	0.3760	-2.86	0.3701	-1.23
0.2641	0.2875	0.4484	298.15	0.3723	0.3801	-2.11	0.3826	-2.76	0.4022	-8.04	0.3845	-3.27	0.3777	-1.45
0.2849	0.3060	0.4091	298.15	0.3786	0.3875	-2.35	0.3900	-3.02	0.4104	-8.39	0.3922	-3.60	0.3848	-1.63
0.3088	0.3222	0.3690	298.15	0.3844	0.3956	-2.91	0.3983	-3.61	0.4192	-9.07	0.4008	-4.26	0.3926	-2.12
0.3330	0.3391	0.3279	298.15	0.3926	0.4040	-2.90	0.4068	-3.63	0.4283	-9.09	0.4097	-4.36	0.4007	-2.06
0.3559	0.3553	0.2888	298.15	0.3996	0.4122	-3.14	0.4152	-3.89	0.4369	-9.33	0.4184	-4.69	0.4086	-2.24
0.3760	0.3735	0.2505	298.15	0.4063	0.4199	-3.35	0.4230	-4.12	0.4448	-9.47	0.4266	-4.98	0.4160	-2.40
0.3983	0.3908	0.2109	298.15	0.4146	0.4284	-3.33	0.4316	-4.11	0.4533	-9.33	0.4355	-5.04	0.4242	-2.31
0.4204	0.3974	0.1822	298.15	0.4233	0.4358	-2.94	0.4391	-3.73	0.4607	-8.84	0.4433	-4.72	0.4313	-1.89
0.4433	0.4045	0.1522	298.15	0.4415	0.4436	-0.47	0.4470	-1.25	0.4685	-6.11	0.4515	-2.27	0.4388	0.61
			APD:			**-2.01**		**-2.65**		**-7.57**		**-3.23**		**-1.31**

3. b) Ternary liquid mixture: Carbontetrachloride + cyclohexane + benzene

x_1	x_2	x_3	T	$\eta/ 10^{-3}$	FST		Wassil		Bingh		K-M		New Approach	
			(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.	η	%Diff.
0.1005	0.2646	0.6349	298.15	0.6823	0.6949	-1.84	0.7084	-3.83	0.7105	-4.14	0.6974	-2.21	0.7099	-4.05
0.1403	0.2246	0.6351	298.15	0.6825	0.6951	-1.85	0.7125	-4.39	0.7107	-4.13	0.6975	-2.20	0.7092	-3.92
0.1751	0.1953	0.6296	298.15	0.6829	0.6968	-2.04	0.7173	-5.04	0.7125	-4.33	0.6992	-2.38	0.7103	-4.01
0.2132	0.1544	0.6324	298.15	0.6928	0.6964	-0.52	0.7201	-3.94	0.7119	-2.75	0.6985	-0.83	0.7089	-2.32
0.2525	0.1240	0.6235	298.15	0.6942	0.6991	-0.70	0.7258	-4.55	0.7147	-2.95	0.7012	-1.00	0.7109	-2.41
0.2911	0.0869	0.6220	298.15	0.6951	0.6998	-0.67	0.7293	-4.92	0.7153	-2.91	0.7017	-0.96	0.7107	-2.25
0.3284	0.0517	0.6199	298.15	0.7159	0.7006	2.13	0.7327	-2.35	0.7161	-0.03	0.7025	1.87	0.7108	0.72
0.3859	0.1812	0.4329	298.15	0.7435	0.7541	-1.43	0.7838	-5.41	0.7709	-3.69	0.7564	-1.74	0.7670	-3.16
0.3461	0.4372	0.217	298.15	0.8223	0.8214	0.11	0.8406	-2.22	0.8337	-1.39	0.8235	-0.14	0.8325	-1.24
APD:						**-0.76**		**-4.07**		**-2.92**		**-1.06**		**-2.52**

CHAPTER – 9

Estimation of thermal conductivity of liquids and liquid mixtures

CHAPTER – 9

Estimation of thermal conductivity of liquids and liquid mixtures

9.1 Introduction

Thermal conductivity in fluids is due to the transfer of momentum from one molecule to another owing the oscillation or collisions of molecules. In many liquids thermal conductivity is greater than low-pressure gases at the same temperature. The thermal conductivity in most of the organic liquids range from 0.1 to 0.17 W/(m.K). Mclaughlin[1] has extensively discussed about the thermal conductivity of fluids. Desprez[2] performed the first experimental and quantitative determination of thermal conductivity. Mclaughlin[3] has explained about the methods and theory for the experimental determination of thermal conductivity. If temperature gradient is applied to fluids, the resulting density gradient will create a buoyancy force, which will be opposed by viscous resistance of the fluids. Due to this reason, experimental measurements of thermal conductivity are difficult, as mechanical equilibrium will be established in the fluids.

Several methods for estimating thermal conductivity and related parameters in fluids are available[4-26]. The predictive methods like Latini method, Sato-Riedel method, Missenard method, Jameson method, Baraconi method, method of Rowley, Li method and many more have been extensively discussed by Reid et at[26]. Pandey and Prajapati[27,28] evaluated the thermal conductivity in monatomic gaseous mixtures, proposing simplified Lindsay-Bromley[9] and Mason-Saxena[13] equations. Pandey et al[29,30] evaluated thermal conductivity of liquids like N_2, Ar and Xe utilising the model proposed by Hirschfelder at al[11]. In these studies, authors have used Flory theory to compute the ultrasonic velocity in liquids, which is required parameter for the relation[11].

The thermal conductivity data of organic liquids finds extensive use in many chemical industries, chiefly in the industries using refrigerants, these days. Le Neindre et al[31-33] have measured thermal conductivity in some fluids including pentafluoroethane (HCF-125), 1,1,1,2-tetrafluoroethane (HCF-134a) and Chlorodifluoromethane (HCFC-22). Workers have purposed an equation to compute

9.1 Introduction

Thermal conductivity in fluids is due to the transfer of momentum from one molecule to another owing the oscillation or collisions of molecules. In many liquids thermal conductivity is greater than low-pressure gases at the same temperature. The thermal conductivity in most of the organic liquids range from 0.1 to 0.17 W/(m.K). Mclaughlin[1] has extensively discussed about the thermal conductivity of fluids. Desprez[2] performed the first experimental and quantitative determination of thermal conductivity. Mclaughlin[3] has explained about the methods and theory for the experimental determination of thermal conductivity. If temperature gradient is applied to fluids, the resulting density gradient will create a buoyancy force, which will be opposed by viscous resistance of the fluids. Due to this reason, experimental measurements of thermal conductivity are difficult, as mechanical equilibrium will be established in the fluids.

Several methods for estimating thermal conductivity and related parameters in fluids are available[4-26]. The predictive methods like Latini method, Sato-Riedel method, Missenard method, Jameson method, Baraconi method, method of Rowley, Li method and many more have been extensively discussed by Reid et at[26]. Pandey and Prajapati[27,28] evaluated the thermal conductivity in monatomic gaseous mixtures, proposing simplified Lindsay-Bromley[9] and Mason-Saxena[13] equations. Pandey et al[29.30] evaluated thermal conductivity of liquids like N_2, Ar and Xe utilising the model proposed by Hirschfelder at al[11]. In these studies, authors have used Flory theory to compute the ultrasonic velocity in liquids, which is required parameter for the relation[11].

The thermal conductivity data of organic liquids finds extensive use in many chemical industries, chiefly in the industries using refrigerants, these days. Le Neindre et al[31-33] have measured thermal conductivity in some fluids including pentafluoroethane (HCF-125), 1,1,1,2-tetrafluoroethane (HCF-134a) and Chlorodifluoromethane (HCFC-22). Workers have purposed an equation to compute

thermal conductivity outside the critical region also. Recently Latini et al[34,35] have proposed a simplified relation for the evaluation of thermal conductivity in the refrigerants of methane, ethane and propane series. The relation has been tested in verities of refrigerants.

In the present work, thermal conductivities of some pure liquids and the liquid mixtures have been computed using the different approaches, than commonly used approaches. Some organic liquids and five organic liquid mixtures at varying conditions are taken under investigation. For the evaluation of thermal conductivity of the pure liquids, Sato-Riedel[26] method has been utilised. But the necessary parameters, the critical constants, have been computed based upon Jobak[24] group contribution method. To the best of our knowledge, this approach has not been used earlier for the evaluation of thermal conductivity. We are especially interested in the present approach, as one needs only the idea of structure of the organic molecules. There is no need of any measured parameters for the evaluation of thermal conductivity of the liquids, using this approach.

Wassiljewa[4] proposed very successful relation for the prediction of transport properties in gaseous mixtures. Wassiljewa and similar relations have been utilised to evaluate thermal conductivity in gaseous mixtures. To the best of our knowledge, this relation has not been utilised to evaluate the thermal conductivity of organic liquid mixtures. The liquids also possess some similarity with gases. The given relation is expected to be suitable for the evaluation of thermal conductivity of liquids also, the reason being, no specific parameters, which differ significantly in liquids and gases, have been involved in the equation. For the evaluation of the adjustable parameter used in Wassiljewa relation, simplified form of Mason and Saxena relation has been employed, which has been utilised elsewhere also[27,28]. The present work may lead to the new approach to determine thermal conductivities of organic liquids and their mixtures. For comparison purpose, Li method[20] has also been utilised for the evaluation of thermal conductivity in liquid mixtures.

thermal conductivity outside the critical region also. Recently Latini et al[34,35] have proposed a simplified relation for the evaluation of thermal conductivity in the refrigerants of methane, ethane and propane series. The relation has been tested in verities of refrigerants.

In the present work, thermal conductivities of some pure liquids and the liquid mixtures have been computed using the different approaches, than commonly used approaches. Some organic liquids and five organic liquid mixtures at varying conditions are taken under investigation. For the evaluation of thermal conductivity of the pure liquids, Sato-Riedel[26] method has been utilised. But the necessary parameters, the critical constants, have been computed based upon Jobak[24] group contribution method. To the best of our knowledge, this approach has not been used earlier for the evaluation of thermal conductivity. We are especially interested in the present approach, as one needs only the idea of structure of the organic molecules. There is no need of any measured parameters for the evaluation of thermal conductivity of the liquids, using this approach.

Wassiljewa[4] proposed very successful relation for the prediction of transport properties in gaseous mixtures. Wassiljewa and similar relations have been utilised to evaluate thermal conductivity in gaseous mixtures. To the best of our knowledge, this relation has not been utilised to evaluate the thermal conductivity of organic liquid mixtures. The liquids also possess some similarity with gases. The given relation is expected to be suitable for the evaluation of thermal conductivity of liquids also, the reason being, no specific parameters, which differ significantly in liquids and gases, have been involved in the equation. For the evaluation of the adjustable parameter used in Wassiljewa relation, simplified form of Mason and Saxena relation has been employed, which has been utilised elsewhere also[27,28.] The present work may lead to the new approach to determine thermal conductivities of organic liquids and their mixtures. For comparison purpose, Li method[20] has also been utilised for the evaluation of thermal conductivity in liquid mixtures.

9.2 Theoretical

One of the most successful empirical equations describing thermal conductivity in gaseous mixture is due to Wassiljewa[4],

$$\lambda = \sum_i \frac{\lambda_i}{1 + \sum_{j \neq i} A_{ij} \frac{x_j}{x_i}} \qquad \ldots(1)$$

where, λ is thermal conductivity of gas mixture, x_i and x_j are the mole fractions of pure components of the mixture and A_{ij} is adjustable parameter. The above equation can be expressed in the convenient form as:

$$\lambda = \sum_i \frac{x_i \lambda_i}{1 + \sum_j A_{ij} x_j} \qquad \ldots(2)$$

The adjustable parameter A_{ij} can be evaluated using simplified Mason and Saxena equation[13] as:

$$A_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j}\right)^{-1/2} \left[1 + \left(\frac{\lambda_i}{\lambda_j}\right)^{1/2} \left(\frac{M_j}{M_i}\right)^{1/4}\right]^2 \qquad \ldots(3)$$

Li[20] proposed the following relation for the estimation of thermal conductivity in liquid mixtures:

$$\lambda = \sum_{i=1}^{n} \sum_{j=1}^{n} \phi_i \phi_j \lambda_{ij} \qquad \ldots(4)$$

where, ϕ_i and ϕ_j are the volume fractions of the components of mixtures and λ_{ij} is given by:

$$\lambda_{ij} = 2\left(\lambda_1^{-1} + \lambda_2^{-1}\right)^{-1} \qquad \ldots(5)$$

For binary system of 1 and 2, eq (4) can be simplified as:

$$\lambda = \phi_1^2 \lambda_1 + 2\phi_1\phi_2 \lambda_{12} + \phi^2_2\lambda_2 \qquad \ldots(6)$$

where, λ_{12} in eq (6) can be deduced from harmonic, geometr
approximations, preferred one being harmonic mean.

al conductivity in

Sato-Riedel method[26] for the evaluation of thermal conductivit
be given as

...(1)

$$\lambda = \frac{\left(1.11/M^{1/2}\right)\left[3+20\,(1-T_r)^{2/3}\right]}{3+20\left[1-T_{br}\right]^{2/3}}$$

ole fractions of

where $T_{br} = T_b/Tc$ and T_b is normal boiling point of liquid. For the above equation
critical constants required here, Jobak[24] relation based upon g
method can be employed. The relation is given as:

...(2)

$$T_c = T_b\left\{0.584+0.965\ \sum\Delta_T - \left(\sum\Delta T\right)^2\right\}^{-1}$$

and T_b can be evaluated using the relation

and Saxena

$$T_b = 198+\sum\Delta_b$$

The values of Δ_T and Δ_b have to be computed based upon the cont
various structures and functional groups in the organic compounds.

...(3)

Besides these relations, there are several other relations also to evaluat
conductivity of fluids and their mixtures, which are beyond the scope c
study.

ivity in

4)

λ_{ij} is

9.3 Results and Discussion

The computed and experimental values of thermal conductivity of some pu
liquids and five liquid mixtures of organic compounds have been recorded
and 3. Some parameters of components

where, λ_{12} in eq (6) can be deduced from harmonic, geometric or arithmetic mean approximations, preferred one being harmonic mean.

Sato-Riedel method[26] for the evaluation of thermal conductivity in pure liquids can be given as

$$\lambda = \frac{\left(1.11/M^{1/2}\right)\left[3+20\,(1-T_r)^{2/3}\right]}{3+20\left[1-T_{br}\right]^{2/3}} \qquad ...(7)$$

where $T_{br} = T_b/Tc$ and T_b is normal boiling point of liquid. For the computation of the critical constants required here, Jobak[24] relation based upon group contribution method can be employed. The relation is given as:

$$T_c = T_b\left\{0.584+0.965\ \sum\Delta_T - \left(\sum\Delta T\right)^2\right\}^{-1} \qquad ...(8)$$

and T_b can be evaluated using the relation

$$T_b = 198+\sum\Delta_b \qquad ...(9)$$

The values of Δ_T and Δ_b have to be computed based upon the contribution due to various structures and functional groups in the organic compounds.

Besides these relations, there are several other relations also to evaluate the thermal conductivity of fluids and their mixtures, which are beyond the scope of the present study.

9.3 Results and Discussion

The computed and experimental values of thermal conductivity of some pure organic liquids and five liquid mixtures of organic compounds have been recorded in table 1 and 3. Some parameters of components and calculated values of adjustable parameters in liquid mixtures have been listed in table-2. The necessary data for computation have been taken from literature[36-42]. Equations (7) and (8) were utilised to evaluate thermal conductivity of pure liquids. The computed and experimental

values of thermal conductivity in the pure liquids have been depicted in table-1. Table-1 also lists the computed values of critical temperature (T_c) and normal boiling point (T_b) of the liquids, with their percentage differences from literature values. The values recorded in table-1 vouch the applicability of the present approach for the evaluation of thermal conductivity in pure organic liquids. Deviations in the case of alkanols and alkanes seem to be high. Still the approach can be considered to be encouraging due to the advantage that no experimental data is required for the case.

The thermal conductivities in liquid mixtures of various organic compounds were computed using eq (2) and (6). Experimental and computed values for the same have been recorded in table-3. As expected, while aiming the present study, Wassiljewa relation is found to give encouraging results in the systems under study. It is interesting to note that eq (2), which was successfully used to compute thermal conductivity of gaseous mixture, is found to give quite satisfactory results in the liquid mixtures of organic compounds also. In most of the cases, Li method and Wassiljewa method are found to be approximate in nature. In some cases like liquid mixture of aqueous glycine + threonine, Wassiljewa relation seems to be better. In contrary, in some cases, like prop-2-enol + ethyl benzene, Li method is found to give better results. These results may authenticate the application of Wassiljewa relation for the computation of thermal conductivity in organic liquid mixtures.

9.4 References

1. Mclaughlin E, *Chem Rev,* **64** (1964) 389.
2. Partington J R, *An Advance Treatise on Phys Chem*, vol. 2, 1950.
3. Mclaughlin E & Pittman J F T, *Phil Trans Roy Soc,* **270** (1971) 557.
4. Wassiljewa A, *Physik Z,* **5** (1904) 737.
5. Enskog D, *Physik Z,* **12** (1911) 533.
6. Chaman S, *Phil Trans A,* **217** (1917) 115.
7. Chapman S G & Cowling T G, *Mathematical Theory of Non- uniform Gases*, Cambridge Univ press, Cambridge, 1939.

values of thermal conductivity in the pure liquids have been depicted in table-1. Table-1 also lists the computed values of critical temperature (T_c) and normal boiling point (T_b) of the liquids, with their percentage differences from literature values. The values recorded in table-1 vouch the applicability of the present approach for the evaluation of thermal conductivity in pure organic liquids. Deviations in the case of alkanols and alkanes seem to be high. Still the approach can be considered to be encouraging due to the advantage that no experimental data is required for the case.

The thermal conductivities in liquid mixtures of various organic compounds were computed using eq (2) and (6). Experimental and computed values for the same have been recorded in table-3. As expected, while aiming the present study, Wassiljewa relation is found to give encouraging results in the systems under study. It is interesting to note that eq (2), which was successfully used to compute thermal conductivity of gaseous mixture, is found to give quite satisfactory results in the liquid mixtures of organic compounds also. In most of the cases, Li method and Wassiljewa method are found to be approximate in nature. In some cases like liquid mixture of aqueous glycine + threonine, Wassiljewa relation seems to be better. In contrary, in some cases, like prop-2-enol + ethyl benzene, Li method is found to give better results. These results may authenticate the application of Wassiljewa relation for the computation of thermal conductivity in organic liquid mixtures.

9.4 References

1. Mclaughlin E, *Chem Rev,* **64** (1964) 389.
2. Partington J R, *An Advance Treatise on Phys Chem*, vol. 2, 1950.
3. Mclaughlin E & Pittman J F T, *Phil Trans Roy Soc,* **270** (1971) 557.
4. Wassiljewa A, *Physik Z,* **5** (1904) 737.
5. Enskog D, *Physik Z,* **12** (1911) 533.
6. Chaman S, *Phil Trans A,* **217** (1917) 115.
7. Chapman S G & Cowling T G, *Mathematical Theory of Non- uniform Gases*, Cambridge Univ press, Cambridge, 1939.

8. Wilke C R, *J Chem Phys,* **18** (1950) 517.
9. Lindsay A L & Bromley L A, *Ind Eng Chem,* **42** (1950) 1508.
10. Riedel L, *Chem Ing Tech,* **21** (1949) 349; 23 (1951) 59.
11. Hirschfelder J O, Curtiss C F & Bird R B, *Molecular Theory of Gases and Liquids*, John Wiley Inc, New York, 1954.
12. Hirschfelder J O & Curtiss C F, *J Chem Phys,* **29** (1958) 361.
13. Mason E A & Saxena S C, *Phys Fluids,* **01** (1958) 361.
14. Mason E A & Saxena S C, J *Chem Phys,* **31** (1959) 511.
15. Cowling T G, *Proc Roy Soc A,* **263** (1961) 186.
16. Wright P G & Gray P, *Trans Farad Soc,* **58** (1962) 1.
17. Cowling T G, Gray P & Wright P G, *Proc Roy Soc A,* **276** (1963) 69.
18. Preston G T, Chapman T W & Prausnitz J M, *Cryogenics,* **7(5)** (1967) 274.
19. Jamieson D T, Irving J B & Tudhope J S, *Liquid Therm Cond Data Survey*, Edinberg, 1975.
20. Li C C, *AIChE J,* **22** (1976) 927.
21. Latini G & Pacetti M, *Therm Conduct,* **15** (1977) 245.
22. Teja A S & Rice P, *Chem Eng Sci,* **36** (1981) 417.
23. Rowling R L, *Chem Eng Sci,* **37** (1982) 897.
24. Jobak K G, *Massachusetts Institute of Technology*, Cambridge, 1984.
25. Baraconi C P, Filippo F D & Latini G, Workshop on *Thermal Conductivity Measurement*, IMEKO, Budapest, 1983.
26. Ried R C, Prausnitz J M. & Poling B E, *The properties of gases and Liquids*, McGrawHill Inc, 1987.
27. Pandey J D & Prajapati S R, *Proc Ind Nat Sci Acad,* **45A** (1979) 372.
28. Prajapati S R & Pandey J D, *Proc Ind Nat Sci Acad,* **47A** (1981) 428.
29. Pandey J D, Chaturedi B R & Pant N, *Acoustic Letters,* **4(7)** (1981) 128.
30. Pandey J D & Dey R, *Ind J Phys,* **74A** (2000) 319.
31. Le Neindre B & Garrabos Y, *Int J Thermophys*, **20** (1999) 375.
32. Le Neindre B & Garrabos Y, *Int J Thermophys*, **20** (1999) 1379.

33. Le Neindre B, Garrabos Y, Sabirzianov A & Goumerov F, *J Chem Eng Data,* **46** (2001) 193.

34. Latini G, Passerini F & Polonara F, *Int J Thermophys,* **20** (1999) 73.

35. Latini G, Grifoni R C, & Passerini G, 13th Symposium on *Thermophysical properties*, Boudler, Colorado, 2000.

36. Venart D E S & Krishnamurthy C, *Proc 7th Conf on Therm Cond*, NBS space Pub, 1967.

37. Zimmerling W & Ratzsch M, *Chem Tech*, **28(2)** (1976) 84.

38. Missenard F A, *Rev Gen Thermodyn*, 141 (1972) 751.

39. Jamieson D T & Tudhope J S, *Natl Eng Lab*, Glassow Rep, 1964.

40. Hyderkhan V & Subramanyam S V, *Trans Farad Soc*, **67** (1971) 2282.

41. Calado C G, Gerald A G & Stavely L A K, *Trans Farad Soc*, **70** (1974) 1445.

42. Delmas G & Turrell S, *Trans Farad Soc*, **70** (1974) 572.

Table - 1

Experimental and computed values of thermal conductivity in pure liquids Computation method: Sato-Riedel (S-R) method in conjunction with group contribution

Liquids	T	λ	Group Contr		Group Contr		S-R+Grp Contr	
	K	$Wm^{-1}K^{-1}$	T_b/ (K)	% Diff	T_c/ (K)	% Diff	$\lambda/Wm^{-1}K^{-1}$	% Diff
Benzene	293	0.148	358.38	-1.47	569.71	-1.34	0.1429	3.42
	323	0.137	358.38	-1.47	569.71	-1.34	0.1345	1.84
Toluene	293	0.135	386.24	-0.64	597.75	-1.01	0.1393	-3.21
p-Xylene	293	0.132	414.10	-0.63	625.12	-1.45	0.1359	-2.97
Cyclohexane	293	0.124	360.90	-2.01	565.41	-2.15	0.1382	-11.46
n-Pentane	293	0.118	313.80	-1.49	476.38	-1.42	0.1371	-16.16
Methanol	293	0.192	314.46	6.88	475.49	7.24	0.2262	-17.81
Ethanol	293	0.165	337.34	4.00	499.11	2.88	0.1939	-17.54
n_Propanol	293	0.156	360.22	2.72	522.27	2.71	0.1768	-13.36
Aniline	293	0.182	435.89	4.74	666.01	4.72	0.1562	14.19
Chloroform	293	0.120	334.13	0.05	532.11	0.80	0.1122	6.50
CCl_4	293	0.104	368.77	-5.39	586.63	-5.40	0.1003	3.52
Chlorobenzene	293	0.130	400.79	1.02	623.15	1.46	0.1302	-0.12
Ethyl Acetate	293	0.147	349.14	0.30	523.60	-0.06	0.1371	6.74
Diethyl Ether	293	0.129	313.34	-1.87	476.89	-2.18	0.1346	-4.31
Acetone	273	0.171	321.91	2.18	500.25	1.55	0.1688	1.26
	313	0.151	321.91	2.18	500.25	1.55	0.1525	-1.02
			APD:	**0.54**		**0.39**		**-2.97**

Table - 1

Experimental and computed values of thermal conductivity in pure liquids Computation method: Sato-Riedel (S-R) method in conjunction with group contribution

Liquids	T	λ	Group Contr		Group Contr		S-R+Grp Contr	
	K	$Wm^{-1}K^{-1}$	T_b/ (K)	% Diff	T_c/ (K)	% Diff	$\lambda/Wm^{-1}K^{-1}$	% Diff
Benzene	293	0.148	358.38	-1.47	569.71	-1.34	0.1429	3.42
	323	0.137	358.38	-1.47	569.71	-1.34	0.1345	1.84
Toluene	293	0.135	386.24	-0.64	597.75	-1.01	0.1393	-3.21
p-Xylene	293	0.132	414.10	-0.63	625.12	-1.45	0.1359	-2.97
Cyclohexane	293	0.124	360.90	-2.01	565.41	-2.15	0.1382	-11.46
n-Pentane	293	0.118	313.80	-1.49	476.38	-1.42	0.1371	-16.16
Methanol	293	0.192	314.46	6.88	475.49	7.24	0.2262	-17.81
Ethanol	293	0.165	337.34	4.00	499.11	2.88	0.1939	-17.54
n_Propanol	293	0.156	360.22	2.72	522.27	2.71	0.1768	-13.36
Aniline	293	0.182	435.89	4.74	666.01	4.72	0.1562	14.19
Chloroform	293	0.120	334.13	0.05	532.11	0.80	0.1122	6.50
CCl_4	293	0.104	368.77	-5.39	586.63	-5.40	0.1003	3.52
Chlorobenzene	293	0.130	400.79	1.02	623.15	1.46	0.1302	-0.12
Ethyl Acetate	293	0.147	349.14	0.30	523.60	-0.06	0.1371	6.74
Diethyl Ether	293	0.129	313.34	-1.87	476.89	-2.18	0.1346	-4.31
Acetone	273	0.171	321.91	2.18	500.25	1.55	0.1688	1.26
	313	0.151	321.91	2.18	500.25	1.55	0.1525	-1.02
			APD:	**0.54**		**0.39**		**-2.97**

Table –2

Various Parameters of binary and ternary liquid mixtures

Liquid Mixtures	T (K)	$V_1/10^{-6}$ $m^3 mol^{-1}$	$V_2/10^{-6}$ $m^3 mol^{-1}$	$\lambda_1/10^{-1}$ W/ (m K)	$\lambda_2/10^{-1}$ W/ (m K)	A_{12}	A_{21}
a) Aqueous Glycine + Alanine	298.15	59.99	72.85	2.562	2.194	1.179	0.851
	303.15	60.48	71.10	2.705	2.336	1.174	0.854
	313.15	60.23	70.88	2.886	2.556	1.159	0.864
b) Aqueous Glycine + Leucine	298.15	59.99	108.85	2.562	1.472	1.786	0.587
	303.15	60.48	108.67	2.705	1.593	1.760	0.593
	313.15	60.23	108.40	2.886	1.790	1.706	0.606
c) Aqueous Glycine + Threonine	298.15	59.99	85.01	2.562	1.626	1.497	0.691
	303.15	60.48	84.94	2.705	1.753	1.479	0.698
	313.15	60.23	84.66	2.886	1.962	1.439	0.712
d) Prop-2-en-ol + Ethyl benzene	298.15	42.33	77.21	2.391	1.227	1.956	0.549
	308.15	42.09	76.98	2.433	1.311	1.898	0.560
e) Prop-2-en-ol + Isopropyl benzene	298.15	42.33	88.96	2.391	1.077	2.255	0.491
	308.15	42.09	88.38	2.4330	1.150	2.187	0.499

Table –2

Various Parameters of binary and ternary liquid mixtures

Liquid Mixtures	T (K)	$V_1/10^{-6}$ $m^3\ mol^{-1}$	$V_2/10^{-6}$ $m^3\ mol^{-1}$	$\lambda_1/10^{-1}$ W/ (m K)	$\lambda_2/10^{-1}$ W/ (m K)	A_{12}	A_{21}
a) Aqueous Glycine +							
Alanine	298.15	59.99	72.85	2.562	2.194	1.179	0.851
	303.15	60.48	71.10	2.705	2.336	1.174	0.854
	313.15	60.23	70.88	2.886	2.556	1.159	0.864
b) Aqueous Glycine +							
Leucine	298.15	59.99	108.85	2.562	1.472	1.786	0.587
	303.15	60.48	108.67	2.705	1.593	1.760	0.593
	313.15	60.23	108.40	2.886	1.790	1.706	0.606
c) Aqueous Glycine +							
Threonine	298.15	59.99	85.01	2.562	1.626	1.497	0.691
	303.15	60.48	84.94	2.705	1.753	1.479	0.698
	313.15	60.23	84.66	2.886	1.962	1.439	0.712
d) Prop-2-en-ol +	298.15	42.33	77.21	2.391	1.227	1.956	0.549
Ethyl benzene	308.15	42.09	76.98	2.433	1.311	1.898	0.560
e) Prop-2-en-ol +	298.15	42.33	88.96	2.391	1.077	2.255	0.491
Isopropyl benzene	308.15	42.09	88.38	2.4330	1.150	2.187	0.499

Table –3

Experimental and Computed values of thermal conductivity in various Binary liquid mixtures

a) Binary Liquid Mixture: Aqueous Glycine + Alanine

x_1	x_2	T	$\lambda/10^{-1}$	Wassiljewa Method		Li Method	
		(K)	W/ (m K)	λ (10^{-1}W/(m K)	% Diff	λ (10^{-1}W/(m K)	% Diff
0.0000	1.0000	298.15	2.1940	2.1940	0.00	2.1940	0.00
0.1170	0.8830	298.15	2.2326	2.2305	0.10	2.2302	0.11
0.2290	0.7710	298.15	2.2643	2.2668	-0.11	2.2663	-0.09
0.3370	0.6630	298.15	2.3671	2.3032	2.70	2.3026	2.73
0.4420	0.5580	298.15	2.2976	2.3400	-1.84	2.3393	-1.81
0.5430	0.4570	298.15	2.3506	2.3767	-1.11	2.3760	-1.08
0.6400	0.3600	298.15	2.3802	2.4133	-1.39	2.4126	-1.36
0.7350	0.2650	298.15	2.4268	2.4506	-0.98	2.4499	-0.95
0.8260	0.1740	298.15	2.4783	2.4875	-0.37	2.4870	-0.35
0.9140	0.0860	298.15	2.5339	2.5245	0.37	2.5243	0.38
1.0000	0.0000	298.15	2.5620	2.5620	0.00	2.5620	0.00
0.0000	1.0000	303.15	2.3360	2.3360	0.00	2.3360	0.00
0.1170	0.8830	303.15	2.3811	2.3728	0.35	2.3734	0.32
0.2290	0.7710	303.15	2.4180	2.4093	0.36	2.4104	0.31
0.3370	0.6630	303.15	2.5125	2.4460	2.65	2.4474	2.59
0.4420	0.5580	303.15	2.4481	2.4829	-1.42	2.4845	-1.49
0.5430	0.4570	303.15	2.4965	2.5198	-0.93	2.5215	-1.00
0.6400	0.3600	303.15	2.5233	2.5565	-1.32	2.5581	-1.38
0.7350	0.2650	303.15	2.5667	2.5937	-1.05	2.5952	-1.11
0.8260	0.1740	303.15	2.6119	2.6307	-0.72	2.6318	-0.76
0.9140	0.0860	303.15	2.6705	2.6676	0.11	2.6682	0.08
1.0000	0.0000	303.15	2.7050	2.7050	0.00	2.7050	0.00
0.0000	1.0000	313.15	2.5560	2.5560	0.00	2.5560	0.00
0.1170	0.8830	313.15	2.6035	2.5895	0.54	2.5894	0.54
0.2290	0.7710	313.15	2.6363	2.6226	0.52	2.6225	0.52
0.3370	0.6630	313.15	2.6987	2.6557	1.59	2.6555	1.60
0.4420	0.5580	313.15	2.6727	2.6890	-0.61	2.6888	-0.60
0.5430	0.4570	313.15	2.7089	2.7220	-0.48	2.7218	-0.48
0.6400	0.3600	313.15	2.7397	2.7548	-0.55	2.7546	-0.54
0.7350	0.2650	313.15	2.7711	2.7879	-0.60	2.7877	-0.60
0.8260	0.1740	313.15	2.8213	2.8206	0.03	2.8204	0.03
0.9140	0.0860	313.15	2.8562	2.8532	0.11	2.8531	0.11
1.0000	0.0000	313.15	2.8860	2.8860	0.00	2.8860	0.00

Table –3

Experimental and Computed values of thermal conductivity in various Binary liquid mixtures

a) Binary Liquid Mixture: Aqueous Glycine + Alanine

x_1	x_2	T	$\lambda/10^{-1}$	Wassiljewa Method		Li Method	
		(K)	W/ (m K)	λ (10^{-1}W/(m K)	% Diff	λ (10^{-1}W/(m K)	% Diff
0.0000	1.0000	298.15	2.1940	2.1940	0.00	2.1940	0.00
0.1170	0.8830	298.15	2.2326	2.2305	0.10	2.2302	0.11
0.2290	0.7710	298.15	2.2643	2.2668	-0.11	2.2663	-0.09
0.3370	0.6630	298.15	2.3671	2.3032	2.70	2.3026	2.73
0.4420	0.5580	298.15	2.2976	2.3400	-1.84	2.3393	-1.81
0.5430	0.4570	298.15	2.3506	2.3767	-1.11	2.3760	-1.08
0.6400	0.3600	298.15	2.3802	2.4133	-1.39	2.4126	-1.36
0.7350	0.2650	298.15	2.4268	2.4506	-0.98	2.4499	-0.95
0.8260	0.1740	298.15	2.4783	2.4875	-0.37	2.4870	-0.35
0.9140	0.0860	298.15	2.5339	2.5245	0.37	2.5243	0.38
1.0000	0.0000	298.15	2.5620	2.5620	0.00	2.5620	0.00
0.0000	1.0000	303.15	2.3360	2.3360	0.00	2.3360	0.00
0.1170	0.8830	303.15	2.3811	2.3728	0.35	2.3734	0.32
0.2290	0.7710	303.15	2.4180	2.4093	0.36	2.4104	0.31
0.3370	0.6630	303.15	2.5125	2.4460	2.65	2.4474	2.59
0.4420	0.5580	303.15	2.4481	2.4829	-1.42	2.4845	-1.49
0.5430	0.4570	303.15	2.4965	2.5198	-0.93	2.5215	-1.00
0.6400	0.3600	303.15	2.5233	2.5565	-1.32	2.5581	-1.38
0.7350	0.2650	303.15	2.5667	2.5937	-1.05	2.5952	-1.11
0.8260	0.1740	303.15	2.6119	2.6307	-0.72	2.6318	-0.76
0.9140	0.0860	303.15	2.6705	2.6676	0.11	2.6682	0.08
1.0000	0.0000	303.15	2.7050	2.7050	0.00	2.7050	0.00
0.0000	1.0000	313.15	2.5560	2.5560	0.00	2.5560	0.00
0.1170	0.8830	313.15	2.6035	2.5895	0.54	2.5894	0.54
0.2290	0.7710	313.15	2.6363	2.6226	0.52	2.6225	0.52
0.3370	0.6630	313.15	2.6987	2.6557	1.59	2.6555	1.60
0.4420	0.5580	313.15	2.6727	2.6890	-0.61	2.6888	-0.60
0.5430	0.4570	313.15	2.7089	2.7220	-0.48	2.7218	-0.48
0.6400	0.3600	313.15	2.7397	2.7548	-0.55	2.7546	-0.54
0.7350	0.2650	313.15	2.7711	2.7879	-0.60	2.7877	-0.60
0.8260	0.1740	313.15	2.8213	2.8206	0.03	2.8204	0.03
0.9140	0.0860	313.15	2.8562	2.8532	0.11	2.8531	0.11
1.0000	0.0000	313.15	2.8860	2.8860	0.00	2.8860	0.00

b) Binary Liquid Mixture: Aqueous Glycine +Leucine

x_1	x_2	T (K)	$\lambda/10^{-1}$ W/(m K)	Wassiljewa Method λ (10^{-1}W/(m K)	% Diff	Li Method λ (10^{-1}W/(m K)	% Diff
0.0000	1.0000	298.15	1.4720	1.4720	0.00	1.4720	0.00
0.1630	0.8370	298.15	1.4773	1.5728	-6.47	1.5776	-6.79
0.3040	0.6960	298.15	1.6879	1.6749	0.77	1.6835	0.26
0.4280	0.5720	298.15	1.8206	1.7790	2.28	1.7903	1.67
0.5380	0.4620	298.15	1.9090	1.8853	1.24	1.8981	0.57
0.6360	0.3640	298.15	2.0287	1.9934	1.74	2.0067	1.08
0.7240	0.2760	298.15	2.1128	2.1036	0.44	2.1163	-0.17
0.8030	0.1970	298.15	2.2581	2.2151	1.90	2.2263	1.41
0.8750	0.1250	298.15	2.3401	2.3292	0.47	2.3376	0.11
0.9400	0.0600	298.15	2.4414	2.4441	-0.11	2.4489	-0.31
1.0000	0.0000	298.15	2.5620	2.5620	0.00	2.5620	0.00
0.0000	1.0000	303.15	1.5930	1.5930	0.00	1.5930	0.00
0.1630	0.8370	303.15	1.6638	1.6976	-2.03	1.7017	-2.28
0.3040	0.6960	303.15	1.8202	1.8031	0.94	1.8105	0.54
0.4280	0.5720	303.15	1.9601	1.9104	2.54	1.9199	2.05
0.5380	0.4620	303.15	2.0496	2.0194	1.47	2.0303	0.94
0.6360	0.3640	303.15	2.1712	2.1300	1.90	2.1412	1.38
0.7240	0.2760	303.15	2.2597	2.2422	0.77	2.2530	0.30
0.8030	0.1970	303.15	2.4109	2.3555	2.30	2.3648	1.91
0.8750	0.1250	303.15	2.4865	2.4708	0.63	2.4779	0.35
0.9400	0.0600	303.15	2.5851	2.5866	-0.06	2.5906	-0.21
1.0000	0.0000	303.15	2.7050	2.7050	0.00	2.7050	0.00
0.0000	1.0000	313.15	1.7900	1.7900	0.00	1.7900	0.00
0.1630	0.8370	313.15	1.9704	1.8968	3.73	1.8970	3.72
0.3040	0.6960	313.15	2.0267	2.0038	1.13	2.0040	1.12
0.4280	0.5720	313.15	2.1672	2.1116	2.56	2.1119	2.55
0.5380	0.4620	313.15	2.2604	2.2204	1.77	2.2206	1.76
0.6360	0.3640	313.15	2.3730	2.3299	1.82	2.3299	1.82
0.7240	0.2760	313.15	2.4663	2.4401	1.06	2.4400	1.07
0.8030	0.1970	313.15	2.6128	2.5505	2.38	2.5503	2.39
0.8750	0.1250	313.15	2.6874	2.6621	0.94	2.6618	0.95
0.9400	0.0600	313.15	2.7764	2.7732	0.11	2.7731	0.12
1.0000	0.0000	313.15	2.8860	2.8860	0.00	2.8860	0.00

c) Binary Liquid Mixture: Aqueous Glycine + Threonine

x_1	x_2	T (K)	$\lambda/10^{-1}$ W/ (m K)	Wassiljewa Method λ (10^{-1}W/(m K)	% Diff	Li Method λ (10^{-1}W/(m K)	% Diff
0.0000	1.0000	298.15	1.6260	1.6260	0.00	1.6260	0.00
0.1560	0.8440	298.15	1.7036	1.7233	-1.16	1.7340	-1.78
0.2840	0.7160	298.15	1.8105	1.8127	-0.12	1.8307	-1.12
0.4050	0.5950	298.15	1.9041	1.9065	-0.13	1.9297	-1.35
0.5140	0.4860	298.15	1.9944	2.0000	-0.28	2.0260	-1.59
0.6130	0.3870	298.15	2.0887	2.0933	-0.22	2.1200	-1.50
0.7040	0.2960	298.15	2.1860	2.1873	-0.06	2.2125	-1.21
0.7870	0.2130	298.15	2.2809	2.2808	0.01	2.3025	-0.95
0.6840	0.3160	298.15	2.3792	2.1659	8.96	2.1917	7.88
0.9350	0.0650	298.15	2.4738	2.4691	0.19	2.4781	-0.17
1.0000	0.0000	298.15	2.5620	2.5620	0.00	2.5620	0.00
0.0000	1.0000	303.15	1.7530	1.7530	0.00	1.7530	0.00
0.1560	0.8440	303.15	1.8368	1.8533	-0.90	1.8637	-1.47
0.2840	0.7160	303.15	1.9463	1.9451	0.06	1.9627	-0.84
0.4050	0.5950	303.15	2.0463	2.0412	0.25	2.0638	-0.85
0.5140	0.4860	303.15	2.1412	2.1366	0.21	2.1619	-0.97
0.6130	0.3870	303.15	2.3368	2.2317	4.50	2.2576	3.39
0.7040	0.2960	303.15	2.3368	2.3271	0.41	2.3516	-0.63
0.7870	0.2130	303.15	2.4323	2.4218	0.43	2.4428	-0.43
0.6840	0.3160	303.15	2.5255	2.3054	8.71	2.3304	7.73
0.9350	0.0650	303.15	2.6266	2.6117	0.57	2.6203	0.24
1.0000	0.0000	303.15	2.7050	2.7050	0.00	2.7050	0.00
0.0000	1.0000	313.15	1.9620	1.9620	0.00	1.9620	0.00
0.1560	0.8440	313.15	1.9450	2.0623	-6.03	2.0694	-6.40
0.2840	0.7160	313.15	2.0585	2.1535	-4.61	2.1654	-5.19
0.4050	0.5950	313.15	2.1574	2.2482	-4.21	2.2635	-4.92
0.5140	0.4860	313.15	2.2530	2.3417	-3.94	2.3587	-4.69
0.6130	0.3870	313.15	2.3479	2.4342	-3.68	2.4516	-4.42
0.7040	0.2960	313.15	2.4418	2.5265	-3.47	2.5428	-4.13
0.7870	0.2130	313.15	2.5344	2.6174	-3.27	2.6314	-3.83
0.6840	0.3160	313.15	2.6289	2.5055	4.69	2.5222	4.06
0.9350	0.0650	313.15	2.7224	2.7980	-2.78	2.8037	-2.99
1.0000	0.0000	313.15	2.8860	2.8860	0.00	2.8860	0.00

c) Binary Liquid Mixture: Aqueous Glycine + Threonine

x_1	x_2	T	$\lambda/10^{-1}$	Wassiljewa Method		Li Method	
		(K)	W/ (m K)	λ (10^{-1}W/(m K)	% Diff	λ (10^{-1}W/(m K)	% Diff
0.0000	1.0000	298.15	1.6260	1.6260	0.00	1.6260	0.00
0.1560	0.8440	298.15	1.7036	1.7233	-1.16	1.7340	-1.78
0.2840	0.7160	298.15	1.8105	1.8127	-0.12	1.8307	-1.12
0.4050	0.5950	298.15	1.9041	1.9065	-0.13	1.9297	-1.35
0.5140	0.4860	298.15	1.9944	2.0000	-0.28	2.0260	-1.59
0.6130	0.3870	298.15	2.0887	2.0933	-0.22	2.1200	-1.50
0.7040	0.2960	298.15	2.1860	2.1873	-0.06	2.2125	-1.21
0.7870	0.2130	298.15	2.2809	2.2808	0.01	2.3025	-0.95
0.6840	0.3160	298.15	2.3792	2.1659	8.96	2.1917	7.88
0.9350	0.0650	298.15	2.4738	2.4691	0.19	2.4781	-0.17
1.0000	0.0000	298.15	2.5620	2.5620	0.00	2.5620	0.00
0.0000	1.0000	303.15	1.7530	1.7530	0.00	1.7530	0.00
0.1560	0.8440	303.15	1.8368	1.8533	-0.90	1.8637	-1.47
0.2840	0.7160	303.15	1.9463	1.9451	0.06	1.9627	-0.84
0.4050	0.5950	303.15	2.0463	2.0412	0.25	2.0638	-0.85
0.5140	0.4860	303.15	2.1412	2.1366	0.21	2.1619	-0.97
0.6130	0.3870	303.15	2.3368	2.2317	4.50	2.2576	3.39
0.7040	0.2960	303.15	2.3368	2.3271	0.41	2.3516	-0.63
0.7870	0.2130	303.15	2.4323	2.4218	0.43	2.4428	-0.43
0.6840	0.3160	303.15	2.5255	2.3054	8.71	2.3304	7.73
0.9350	0.0650	303.15	2.6266	2.6117	0.57	2.6203	0.24
1.0000	0.0000	303.15	2.7050	2.7050	0.00	2.7050	0.00
0.0000	1.0000	313.15	1.9620	1.9620	0.00	1.9620	0.00
0.1560	0.8440	313.15	1.9450	2.0623	-6.03	2.0694	-6.40
0.2840	0.7160	313.15	2.0585	2.1535	-4.61	2.1654	-5.19
0.4050	0.5950	313.15	2.1574	2.2482	-4.21	2.2635	-4.92
0.5140	0.4860	313.15	2.2530	2.3417	-3.94	2.3587	-4.69
0.6130	0.3870	313.15	2.3479	2.4342	-3.68	2.4516	-4.42
0.7040	0.2960	313.15	2.4418	2.5265	-3.47	2.5428	-4.13
0.7870	0.2130	313.15	2.5344	2.6174	-3.27	2.6314	-3.83
0.6840	0.3160	313.15	2.6289	2.5055	4.69	2.5222	4.06
0.9350	0.0650	313.15	2.7224	2.7980	-2.78	2.8037	-2.99
1.0000	0.0000	313.15	2.8860	2.8860	0.00	2.8860	0.00

d) Binary Liquid Mixture: Prop-2-en-ol + Ethyl benzene

x_1	x_2	T	$\lambda/10^{-1}$	Wassiljewa Method		Li Method	
		(K)	W/ (m K)	λ (10^{-1}W/(m K)	% Diff	λ (10^{-1}W/(m K)	% Diff
0.0000	1.0000	298.15	1.2270	1.2270	0.00	1.2270	0.00
0.1746	0.8254	298.15	1.4035	1.3327	5.05	1.3480	3.96
0.3464	0.6536	298.15	1.5859	1.4602	7.93	1.4891	6.11
0.4789	0.5211	298.15	1.6838	1.5798	6.18	1.6170	3.97
0.6762	0.3238	298.15	1.8605	1.8062	2.92	1.8483	0.65
0.7705	0.2295	298.15	1.9654	1.9423	1.17	1.9812	-0.81
0.8753	0.1247	298.15	2.0274	2.1227	-4.70	2.1509	-6.09
0.9437	0.0563	298.15	2.1544	2.2614	-4.97	2.2768	-5.68
1.0000	0.0000	298.15	2.3910	2.3910	0.00	2.3910	0.00
0.0000	1.0000	308.15	1.3110	1.3110	0.00	1.3110	0.00
0.1746	0.8254	308.15	1.5491	1.4162	8.58	1.4273	7.86
0.3464	0.6536	308.15	1.6539	1.5423	6.75	1.5631	5.49
0.4789	0.5211	308.15	1.7234	1.6596	3.70	1.6862	2.16
0.6762	0.3238	308.15	1.9056	1.8792	1.39	1.9091	-0.19
0.7705	0.2295	308.15	2.0004	2.0098	-0.47	2.0373	-1.85
0.8753	0.1247	308.15	2.1149	2.1812	-3.14	2.2011	-4.07
0.9437	0.0563	308.15	2.1932	2.3119	-5.41	2.3226	-5.90
1.0000	0.0000	308.15	2.4330	2.4330	0.00	2.4330	0.00



d) Binary Liquid Mixture: Prop-2-en-ol + Ethyl benzene

x_1	x_2	T	$\lambda/10^{-1}$	Wassiljewa Method		Li Method	
		(K)	W/ (m K)	λ (10^{-1}W/(m K)	% Diff	λ (10^{-1}W/(m K)	% Diff
0.0000	1.0000	298.15	1.2270	1.2270	0.00	1.2270	0.00
0.1746	0.8254	298.15	1.4035	1.3327	5.05	1.3480	3.96
0.3464	0.6536	298.15	1.5859	1.4602	7.93	1.4891	6.11
0.4789	0.5211	298.15	1.6838	1.5798	6.18	1.6170	3.97
0.6762	0.3238	298.15	1.8605	1.8062	2.92	1.8483	0.65
0.7705	0.2295	298.15	1.9654	1.9423	1.17	1.9812	-0.81
0.8753	0.1247	298.15	2.0274	2.1227	-4.70	2.1509	-6.09
0.9437	0.0563	298.15	2.1544	2.2614	-4.97	2.2768	-5.68
1.0000	0.0000	298.15	2.3910	2.3910	0.00	2.3910	0.00
0.0000	1.0000	308.15	1.3110	1.3110	0.00	1.3110	0.00
0.1746	0.8254	308.15	1.5491	1.4162	8.58	1.4273	7.86
0.3464	0.6536	308.15	1.6539	1.5423	6.75	1.5631	5.49
0.4789	0.5211	308.15	1.7234	1.6596	3.70	1.6862	2.16
0.6762	0.3238	308.15	1.9056	1.8792	1.39	1.9091	-0.19
0.7705	0.2295	308.15	2.0004	2.0098	-0.47	2.0373	-1.85
0.8753	0.1247	308.15	2.1149	2.1812	-3.14	2.2011	-4.07
0.9437	0.0563	308.15	2.1932	2.3119	-5.41	2.3226	-5.90
1.0000	0.0000	308.15	2.4330	2.4330	0.00	2.4330	0.00



e) Binary Liquid Mixture: Prop-2-en-ol + Isopropyl benzene

x_1	x_2	T	$\lambda/10^{-1}$	Wassiljewa Method		Li Method	
		(K)	W/ (m K)	λ (10^{-1}W/(m K)	% Diff	λ (10^{-1}W/(m K)	% Diff
0.0000	1.0000	298.15	1.0770	1.0770	0.00	1.0770	0.00
0.0510	0.9490	298.15	1.1847	1.1050	6.73	1.1098	6.33
0.1204	0.8796	298.15	1.2213	1.1460	6.16	1.1574	5.24
0.2051	0.7949	298.15	1.2767	1.2014	5.90	1.2207	4.39
0.2976	0.7024	298.15	1.3403	1.2698	5.26	1.2975	3.20
0.4435	0.5565	298.15	1.4577	1.3985	4.06	1.4383	1.33
0.5523	0.4477	298.15	1.5414	1.5163	1.63	1.5630	-1.40
0.6437	0.3563	298.15	1.6589	1.6343	1.48	1.6844	-1.54
0.7360	0.2640	298.15	1.7720	1.7766	-0.26	1.8262	-3.06
0.8289	0.1711	298.15	1.9027	1.9504	-2.51	1.9934	-4.77
0.8973	0.1027	298.15	2.0097	2.1041	-4.70	2.1362	-6.30
0.9479	0.0521	298.15	2.1003	2.2358	-6.45	2.2549	-7.36
1.0000	0.0000	298.15	2.3910	2.3910	0.00	2.3910	0.00
0.0000	1.0000	308.15	1.1500	1.1500	0.00	1.1500	0.00
0.0510	0.9490	308.15	1.2633	1.1783	6.73	1.1820	6.43
0.1204	0.8796	308.15	1.2996	1.2197	6.15	1.2285	5.47
0.2051	0.7949	308.15	1.3541	1.2755	5.80	1.2904	4.70
0.2976	0.7024	308.15	1.4186	1.3440	5.26	1.3654	3.75
0.4435	0.5565	308.15	1.5363	1.4724	4.16	1.5030	2.17
0.5523	0.4477	308.15	1.6196	1.5891	1.88	1.6248	-0.32
0.6437	0.3563	308.15	1.7354	1.7052	1.74	1.7434	-0.46
0.7360	0.2640	308.15	1.8460	1.8442	0.10	1.8818	-1.94
0.8289	0.1711	308.15	1.9731	2.0126	-2.00	2.0451	-3.65
0.8973	0.1027	308.15	2.0757	2.1604	-4.08	2.1844	-5.24
0.9479	0.0521	308.15	2.1595	2.2860	-5.86	2.3002	-6.52
1.0000	0.0000	308.15	2.4330	2.4330	0.00	2.4330	0.00

LIST OF PUBLICATIONS

Published

1. J. D. Pandey, Ranjan Dey and **Bishan Datt Bhatt**, "Applicability of thermoacoustical parameters for the computation of available volume in liquid systems", *PhysChemComm* (RSC Journal), **5(6)** (2002) 37.
2. V. Krishna, P. K. Shukla and **Bishan Datt Bhatt**, "Evaluation of ultrasonic velocity in liquid metals using statistical mechanical theory", *Univ. Alld. Stud. (New Millenium Series)*, **1(1)** (2002) 25.

In Press

3. R. S. Singh, V. K. Singh, Amit Pandey and **Bishan Datt Bhatt**, "Studies of viscous properties of binary liquid mixtures", *International Academy of Physical Sciences (Ind)*, 2001
4. R. S. Singh, V. K. Singh, **Bishan Datt Bhatt** and Amit Pandey, "Deviation in some thermodynamic properties of fluorocarbon mixtures", *International Academy of Physical Sciences (Ind)*, 2001.

Communicated

5. J. D. Pandey and **Bishan Datt Bhatt**, "Ultrasonic and refractometric studies in liquid mixtures comprising ethanol, N,N- dimethylformamide and cyclohexane at 308.15 K", *J Chem Eng Data*, 2002.
6. J. D. Pandey and **Bishan Datt Bhatt**, "Excess molar volume and excess isentropic compressibility in liquid mixtures", *J Soln Chem*, 2002.